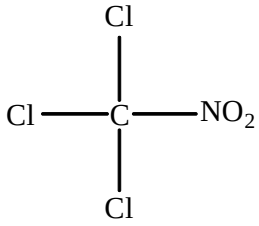
EVALUATION OF CHLOROPICRIN AS A TOXIC AIR CONTAMINANT



PART A

Environmental Fate Review and Exposure Assessment

DRAFT

Worker Health and Safety Branch

Department of Pesticide Regulation

California Environmental Protection Agency

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PUBLIC EXPOSURE TO AIRBORNE CHLOROPICRIN IN CALIFORNIA

HS-1846

By

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ABBREVIATIONS AND ACRONYMS

ADD	Absorbed Daily Dosage
AADD	Annual Average Daily Dosage
AI	active ingredient
ARB	California Air Resources Board
CCR	California Code of Regulations
CFR	Code of Federal Regulations
CMTF	Chloropicrin Manufacturers Task Force
CV	coefficient of variation
DPR	California Department of Pesticide Regulation
FIFRA	Federal Insecticide, Fungicide, and Rodenticide Act
ISCST3	Industrial Source Complex Short Term model, Version 3
LOD	limit of detection
LOQ	limit of quantification
PISP	Pesticide Illness Surveillance Program
PPE	personal protective equipment
PUR	Pesticide Use Report
REI	restricted entry interval
RUP	Restricted Use Pesticide
TAC	toxic air contaminant
TWA	time-weighted average
U.S. EPA	U.S. Environmental Protection Agency

ABSTRACT

This document summarizes available information, data, and calculations of potential airborne exposures to chloropicrin for bystanders (individuals near an application site but not directly involved with the application) and the general population. Potential exposures to chloropicrin in areas adjacent to applications sites are anticipated to equal or exceed all potential airborne exposures in ambient air away from applications, and bystander exposure estimates were used to represent ambient air exposures to chloropicrin. Although bystanders might potentially be exposed to a range of chloropicrin concentrations, for screening risk assessment purposes the highest realistic exposures to bystanders are reported in this exposure assessment.

This document was prepared as part of the process to determine whether chloropicrin meets the criteria to be listed as a Toxic Air Contaminant. Chloropicrin is a fumigant used in California for pre-plant soil fumigations, structural fumigations, and space fumigations. It may be used alone, or mixed with other fumigants such as methyl bromide and 1,3-dichloropropene. When mixed with other fumigants, chloropicrin may be considered either as an active ingredient contributing to pest control, or in smaller amounts as a warning agent to alert individuals in the area to the presence of other fumigants, some of which are odorless. Primary toxic effects that have been associated with exposure to chloropicrin vapor include irritation to eyes and respiratory tract.

Exposure estimates for individuals next to fields during or following chloropicrin applications are reported as concentrations. Although several air monitoring studies have been conducted adjacent to the use of chloropicrin as a pre-plant soil fumigant, either alone or in combination with other fumigants, for several reasons including weather conditions and small field sizes, resulting concentrations did not represent potential realistic upper-bound bystander exposures and estimates were instead calculated from concentrations based on air dispersion modeling of direct flux measurements during application site monitoring. Short-term exposure estimates for bystanders were as follows: 110,000 $\mu g/m^3$ (16,000 ppb) for 1-hour exposures, 44,000 $\mu g/m^3$ (6,500 ppb) for 8-hour exposures, and 7,400 $\mu g/m^3$ (1,100 ppb) for 24-hour exposures. Seasonal bystander exposure was estimated at 490 $\mu g/m^3$ (73 ppb), annual exposure was estimated at 160 $\mu g/m^3$ (24 ppb), and the lifetime exposure estimate was 70 $\mu g/m^3$ (10 ppb).

Exposures of bystanders adjacent to a structural fumigation with chloropicrin as a warning agent were estimated at 73 $\mu g/m^3$ (11 ppb) for a 1-hour duration, 16 $\mu g/m^3$ (2.4 ppb) for an 8-hour exposure, and 6.2 $\mu g/m^3$ (0.92 ppb) for a 24-hour exposure. Exposures of bystanders adjacent to an enclosed space fumigation with chloropicrin were estimated at 2,400 $\mu g/m^3$ (360 ppb) for a 1-hour duration, 680 $\mu g/m^3$ (100 ppb) for an 8-hour exposure, and 210 $\mu g/m^3$ (31 ppb) for a 24-hour exposure; annual and lifetime exposure estimates were both 1.2 $\mu g/m^3$ (0.18 ppb). These concentrations were based on monitoring conducted during a structural fumigation with chloropicrin as a warning agent. Indoor air monitoring following fumigation and aeration in the same study was used to estimate exposure of 140 $\mu g/m^3$ (21 ppb) for a 24-hour duration for individuals returning to fumigated structures. No seasonal, annual, or

lifetime bystander or indoor air exposures from structural fumigation activities are anticipated.

INTRODUCTION

Chloropicrin (trichloronitromethane) is used as either a fumigant or a warning agent. As a fumigant, chloropicrin is used alone or mixed with other fumigants (e.g., methyl bromide, 1,3-dichloropropene). In fumigation, pesticide gas completely fills an area, such as a building or soil in a field, and poisons targeted pests. Chloropicrin controls soil pathogens, certain weeds, and nematodes that adversely affect crops such as strawberries (Duniway, 2002).

As a warning agent, chloropicrin is combined in relatively low concentrations with a fumigant such as methyl bromide or sulfuryl fluoride. A warning agent is a chemical with good warning properties, including odor or irritation, that can be mixed with other chemicals to allow an average person with normal sensory perception to detect the presence of the warning agent at concentrations below which both chemicals produce adverse effects (NIOSH, 1987). Chloropicrin causes transient eye and mucous membrane irritation at relatively low concentrations. As a warning agent, chloropicrin is intended to protect individuals from potentially serious injuries that exposure to a less-detectable fumigant might cause.

The California Department of Pesticide Regulation (DPR) prepared this exposure assessment as part of the determination whether chloropicrin meets the criteria to be listed as a Toxic Air Contaminant. California has laws intended to limit ambient air concentrations of pesticides, including the Toxic Air Contaminants Act (California Health and Safety Code, Sections 39650-39761), which codified the state program to evaluate and control toxic air contaminants (TAC). A pesticide is placed on the TAC list if its concentrations in ambient air are within an order of magnitude of the concentration which has been determined to be adequately protective of human health (California Code of Regulations Title 3 (3 CCR), Section 6890). Chloropicrin is a candidate for inclusion on the TAC list (Helliker, 2002).

Primarily, this exposure assessment estimates airborne exposures to chloropicrin during its use as a pesticidal active ingredient (AI). Additionally, this document contains sections that discuss potential exposures due to chloropicrin use as a warning agent. A comprehensive exposure assessment is in preparation, and will address all anticipated exposure scenarios in addition to public and occupational bystander exposures covered here, including occupational handler and reentry scenarios, and residential reentry scenarios. Previously, DPR prepared exposure assessments for three fumigants that are mixed with chloropicrin: 1,3-dichloropropene, sulfuryl fluoride, and methyl bromide (Sanborn and Powell, 1994; Thongsinthusak and Haskell, 2002; Cochran and DiPaolo, 2005). Also, DPR is drafting an exposure assessment for methyl iodide, a fumigant mixed with chloropicrin that has been proposed for registration in California. Exposure assessments for other fumigants do not address exposures to chloropicrin.

On October 16, 2001, DPR placed all products containing chloropicrin into reevaluation (Cortez, 2001), in accordance with Title 3, Section 6158 of the California Code of

Regulations (3 CCR 6158). The reevaluation decision was based on data suggesting that chloropicrin had the potential to cause adverse health effects at low doses.

The mode of toxic action of chloropicrin is not well characterized. Chloropicrin causes irritation and localized cellular lesions, and available data suggest that these might occur following reaction of chloropicrin with various thiol proteins (i.e., proteins with a sulfhydryl (–SH) functional group), including certain dehydrogenases that have critical sulfhydryl groups in their active sites (Sparks *et al.*, 2000).

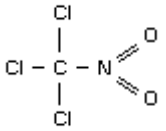
U.S. EPA STATUS

The U.S. Environmental Protection Agency (U.S. EPA) classified chloropicrin as a Toxicity Category I pesticide for acute oral, dermal, and inhalation toxicity (Reaves and Smith, 2008). Due to acute inhalation toxicity, all products containing more than 2% chloropicrin are classified by U.S. EPA as Restricted Use Pesticides (RUPs), which may only be used under the supervision of a certified applicator (Title 40 Code of Federal Regulations (40 CFR), Section 152.175). In July 2008, U.S. EPA released its final revised human health risk assessment and the Reregistration Eligibility Decision for chloropicrin (Reaves and Smith, 2008; U.S. EPA, 2008).

PHYSICOCHEMICAL PROPERTIES

Chloropicrin has a molecular weight of 164.38, and a molecular formula of CCl_3NO_2. Its CAS Number is 76-06-2. The chemical structure is shown in Figure 1.

Figure 1. Chloropicrin Chemical Structure



Several physical and chemical properties of chloropicrin are listed in Table 1. The melting and boiling points indicate that chloropicrin is a liquid under typical use conditions. Chloropicrin is quite volatile (suggesting that inhalation is the major route of exposure) and highly water-soluble. It is non-flammable, and has a vapor density of 5.7, compared to the reference value of 1.0 assigned to air (Meister and Sine, 2003).

The log K_{ow} for chloropicrin is reported as 2.43 (Secara, 1991). Voliva (1987) reported a vapor pressure of 23.2 mm Hg at 25°C. The Henry's Law constant, based on these values, is 2.51×10^{-3} atm-m^3/mole (calculated by DPR's Environmental Monitoring Branch, internal database). Worthington and Wade (2007) reported an empirical Henry's Law constant of 2.1×10^{-3} atm-m^3/mole, measured with a stripping method in which nitrogen was bubbled through a saturated chloropicrin solution in deionized water maintained at 25°C.

Chloropicrin concentrations reported in $\mu g/m^3$ can be converted to equivalent concentrations in parts per billion (ppb), expressed as ratio of weight of chloropicrin to volume of air, using the ideal gas law. At 1 atmosphere of pressure and a temperature of 25°C, the concentration in ppb is equal to the concentration in $\mu g/m^3$, multiplied by 24.45 liter-atm/mole and divided by the molecular weight of 164.38 g/mole. As 24.45/164.38 = 0.1487, this value can be multiplied by the concentration in $\mu g/m^3$ to obtain the concentration in ppb.

Table 1. Physical and Chemical Properties of Chloropicrin

Chemical Property [a]	Value
Melting Point (°C)	-64
Boiling Point (°C)	112
Density (g/ml)	1.656
Water Solubility (mg/L, 25 °C)	2,000
Octanol/Water Partition Coefficient	269
Vapor Pressure (mm Hg, 25 °C)	23.2
Vapor Density	5.7
Henry's Law Constant (atm-m^3/mole, 25 °C)	0.00251
Flash Point	None

[a] DPR Environmental Monitoring Pesticide Chemistry Database; Ariano (1987); Voliva (1987); Secara, 1991; Sparacino (1994); Meister and Sine (2003)

FORMULATIONS AND USES

As of May 2009, there are 54 registered products containing chloropicrin in California, including seven products intended solely for manufacturing or reformulation use and eight products where chloropicrin is used as a warning agent (Table 2). Chloropicrin-containing products are available in both pressurized and non-pressurized containers, as compressed liquids in cylinders or liquid solutions containing emulsifiers. Many are mixtures with methyl bromide or 1,3-dichloropropene. New products have been submitted for registration in California that are mixtures of chloropicrin and methyl iodide.

Table 2 summarizes products available for agricultural and structural/enclosed space use in California. The seven products intended solely for manufacturer use are omitted from Table 2, and are outside the scope of this exposure assessment because manufacturing uses are not regulated by DPR. In structural fumigations, chloropicrin is only used as a warning agent. Enclosed space fumigations with chloropicrin may be done in fumigation of empty potato storage cellars/houses, and grain bins. U.S. EPA has received requests to cancel the space fumigation uses (U.S. EPA, 2008).

Pre-plant soil fumigation is done for many crops, using injection equipment or drip irrigation (five methyl bromide products, containing between 0.5% and 10.5% chloropicrin, have directions for hot gas fumigation; otherwise, chemigation is via cold gas methods). DPR (2004) describes three main types of pre-plant soil fumigation: broadcast fumigation (where

the application of a pesticide occurs uniformly over the area to be treated without regard to arrangement of crops as in rows); strip fumigation (applications that have alternating fumigated and unfumigated areas, often with prior or subsequent fumigation of the unfumigated areas); and bed fumigation (where pre-formed beds are fumigated and the furrows are not). For both strip and bed fumigations, application rates refer only to treated areas; for example, if the maximum application rate is 500 lbs AI/acre (562 kg/ha), and a strip or bed fumigation of a field results in treatment of only 50% of a field in a particular application, then the rate to the field is decreased by 50% to 250 lbs AI/acre (DPR, 2004). This effective broadcast rate is calculated by dividing the mass of AI applied by the area of the entire field, including both treated and untreated areas.

Crops for which some chloropicrin-containing products are registered as preplant fumigants include asparagus, broccoli, cauliflower, eggplant, grapes, lettuce, melons, onions, peppers, pineapple, strawberries, tomatoes, floral crops, nursery crops, and fruit and nut crops. In addition, some products have instructions for fumigation of potting soil, mushroom casing soil, greenhouse beds, seedbeds and seed flats.

Table 2. Chloropicrin-Containing Products in California as of May 2009

Active Ingredient [a]	Number of Products [b]	Chloropicrin Concentration Range (%)	Fumigation Type [c]	Number of Products with Greenhouse Uses [d]
Methyl Bromide	25	0.25 – 67	Soil/Structural [e]	19
Chloropicrin 0.25 – 10.5% [f]	(8)	0.25 – 10.5	Soil/Structural	8
Chloropicrin 19.8 – 67%	(17)	19.8 – 67	Soil	11
Methyl Iodide	0 [g]	2 – 75	Soil	0
1,3-Dichloropropene	13	15 – 60	Soil	0
Chloropicrin as sole AI	9	94 - 100	Soil/Structural [h]	8
Total	47			

[a] Active ingredient (AI) in addition to chloropicrin.
[b] Seven products intended for manufacture use only (i.e., no pesticidal uses) were omitted.
[c] Soil may be fumigated outdoors (e.g., pre-plant fields or replant tree holes), or indoors in greenhouses unless specifically prohibited.
[d] Includes products where greenhouse use is not specifically prohibited by product label. In most cases, specific instructions are provided for soil fumigation in greenhouses. Chloropicrin can be used as a warning agent in greenhouse space fumigation; five products have such directions.
[e] Two methyl bromide products, containing chloropicrin at 0.5 – 2% concentration, provide directions for structural, transport, and space fumigation. All other methyl bromide products are for soil fumigation only.
[f] In these products, chloropicrin is considered a warning agent, and is listed on the label as an "other ingredient" or an "inert ingredient." Chloropicrin at higher concentrations is listed as an active ingredient.
[g] Six products containing chloropicrin with methyl iodide (iodomethane) have been proposed for registration in California.
[h] Sulfuryl fluoride product labels provide instructions for using chloropicrin as a warning agent, which is required for sulfuryl fluoride structural fumigations. Five of the nine chloropicrin product labels also contain directions for use as a warning agent in structural fumigations, and one product label gives enclosed-space fumigation directions.

Chloropicrin as a Warning Agent

When used as a warning agent in a methyl bromide product, the chloropicrin concentration in the product is typically less than 2%. The exception is a product containing 10.5% chloropicrin as a warning agent. When chloropicrin is used as a warning agent for sulfuryl fluoride in structural fumigation, the two chemicals are handled separately; chloropicrin may also be handled separately as a warning agent for structural fumigation with methyl bromide. Warning agents are not typically included when commodity fumigations are done with methyl bromide or sulfuryl fluoride, and no chloropicrin-containing products are registered for use in commodity fumigations (U.S. EPA, 2005). Methyl bromide products containing chloropicrin as a warning agent are included in Table 2.

In this exposure assessment, the only warning agent uses of chloropicrin that are explicitly addressed are those associated with structural fumigation; because of the relative amounts of chloropicrin applied, bystanders adjacent to soil fumigations with methyl bromide containing chloropicrin as a warning agent are anticipated to be exposed to lower chloropicrin concentrations than bystanders adjacent to soil fumigations in which chloropicrin is an AI, and for screening risk assessment purposes the highest realistic exposures to bystanders are reported in this exposure assessment. When completed, the comprehensive exposure assessment will include exposure estimates for soil fumigations with chloropicrin as a warning agent.

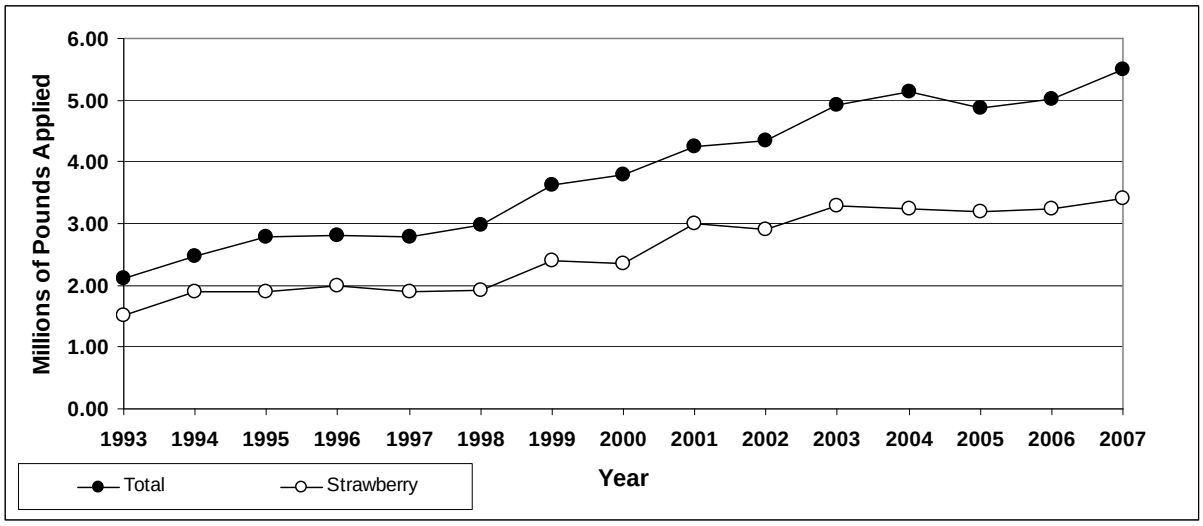
PESTICIDE USE

California requires reporting of all agricultural applications of pesticides, as well as other uses when pesticides are applied by a licensed applicator. These data are collected in the Pesticide Use Report (PUR) database. Figure 2 summarizes use reported in pounds applied in California over the 15-year interval 1993 – 2007. During that time, use increased from 2,494,606 pounds (1,133,912 kg) to 5,494,541 pounds (2,497,519 kg). The majority of use was for pre-plant fumigation of strawberry fields, which accounted for an average of 68% of pounds applied during the 15-year interval. The total number of acres treated with chloropicrin has not increased, however, ranging from 42,702 in 1993 to 61,323 acres in 1999, and averaging 53,974 acres, with strawberry fields averaging 43% of acres treated with chloropicrin during the 15-year interval (data not shown).

In 2007, there were 172,163,465 pounds (78,256,120 kg) of pesticidal AIs reported to be used in California (DPR, 2008). Of this, chloropicrin accounted for 5,494,541 pounds (2,497,519 kg), or 3.2%. Table 3 summarizes PUR data for chloropicrin in the most recent 5-year interval for which data are available, 2003 – 2007, based on pounds AI applied.

Table 3 shows that more than 99% of chloropicrin use is for pre-plant soil fumigation. As with the 15-year interval described above, the greatest use during these five years was in strawberry fields, which accounted for an average of about 64% of total chloropicrin use in the 5-year interval. The top five counties in which chloropicrin was used in the 5-year interval 2003 – 2007 are Monterey, Ventura, Santa Barbara, Santa Cruz, and Siskiyou; together, they accounted for 76% of statewide use.

Figure 2. Chloropicrin Use Reported in California [a]



[a] Use reported in pound applied annually, statewide. Data summarized from the Pesticide Use Report (PUR) database (DPR, 2009). Closed circles represent total chloropicrin use, and open circles represent chloropicrin applied to strawberry fields as a pre-plant fumigant.

Table 3. Chloropicrin Use in California, 2003- 2007

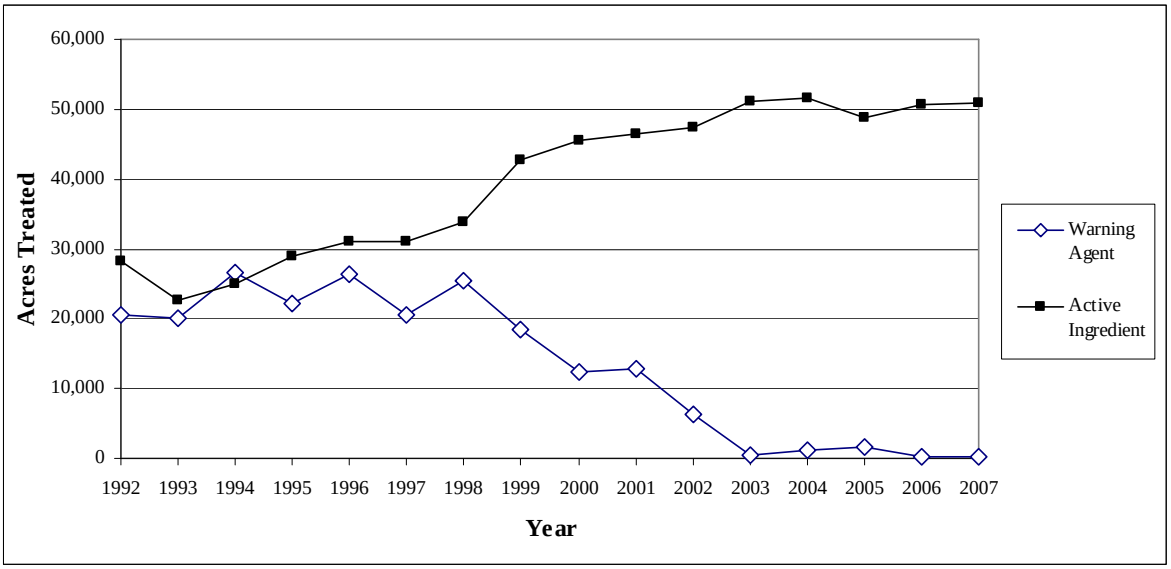
Use Site	Pounds Applied [a]				
	2003	2004	2005	2006	2007
Soil fumigation, preplant [b]	4,882,373	5,110,119	4,862,466	5,017,305	5,488,746
• Strawberries	3,282,719	3,258,348	3,182,417	3,236,844	3,408,331
• (Strawberry % of soil) [c]	(67.2%)	(63.8%)	(65.4%)	(64.5%)	(62.0%)
• Tree crops [d]	16,103	34,363	38,403	23,342	68,762
Commodity fumigation [e]	50	1,048	396	359	734
• Non-research commodity [f]	13	5	0	0	0
Turf/Sod	10,328	12,618	40,008	4,913	15,911
Structural Pest Control	19,939	6,540	2,093	1,126	4,316
Total Pounds Used	4,927,125	5,110,119	4,864,930	5,018,831	5,494,541
Soil fumigation % of total [g]	99.1%	99.5%	99.9%	100%	100%

[a] From DPR (2005a; 2006a; 2006b; 2007; 2008). Multiply values by 0.455 to get use in kg applied. Average use during 5-year interval: 5,088,163 lbs (2,312,801 kg).
[b] Includes all use listed under specific crops, as well as non-specific pre-plant fumigations. Totals include applications to strawberries and tree crops, which are also listed separately for the reasons given below.
[c] Percent of chloropicrin use for pre-plant soil fumigation reported in strawberry beds or fields. Pre-plant soil fumigation for strawberries is the greatest single use of chloropicrin.
[d] Tree crops can be fumigated by handwand as well as by other soil fumigation methods.
[e] Includes commodity fumigation done for research purposes.
[f] Use reported for commodity fumigation, but not reported as research.
[g] Percent of total reported chloropicrin use that was due to pre-plant soil fumigation.

Chloropicrin as a Warning Agent

A query of the PUR database by percent chloropicrin in reported products allowed an estimate of how much agricultural chloropicrin use involved chloropicrin as a warning agent rather than as an AI (DPR, 2009). Figure 3 summarizes PUR data for chloropicrin applied for agricultural uses. Only uses reported as agricultural (rather than non-agricultural) are included in Figure 3, which summarizes uses reported as acres treated (other uses, reported as square feet treated, or miscellaneous treatments such as bins or tree holes, were omitted). These uses include more than 99% of soil fumigant treatments involving chloropicrin. In Figure 3, applications of products containing 0.5 – 2.0% chloropicrin were classified as "warning agent" chloropicrin uses, and applications of products containing more than 2.0% chloropicrin were considered "active ingredient" uses (no use of the product containing 10.5% chloropicrin was reported in the PUR). Both the decrease in warning agent uses and the increase in active ingredient uses are almost certainly related to the decrease of methyl bromide use occurring as a result of the federally-mandated phase-out of methyl bromide use (U.S. EPA, 1993).

Figure 3. Chloropicrin Agricultural Uses in California Reported as Acres Treated [a]



[a] Acres treated annually, statewide, with chloropicrin-containing products in which chloropicrin is up to 2.0% of product formulation (warning agent) or more than 2.0% (active ingredient). Data summarized from the Pesticide Use Report (PUR) database (DPR, 2009). Only agricultural uses are included, and only those uses reported in the PUR database by acres treated (pounds chloropicrin applied would vary between products). To convert acres to hectares (ha), multiply value by 0.405.

REPORTED ILLNESSES

DPR's Worker Health and Safety Branch (WHS) includes a Pesticide Illness Surveillance Program (PISP). PISP maintains a database of all reports of illness and injury potentially related to pesticide exposure in California. The PISP database contains information about the nature of the pesticide exposure and the subsequent illness or injury. DPR uses the database

to identify high-risk situations and to evaluate the effectiveness of DPR's pesticide safety regulatory programs (WHS, 2007).

PISP defines a "case" as the program's representation of a pesticide exposure and its apparent effects on one individual's health (WHS, 2007). PISP scientists evaluate investigations of each case and record a qualitative assessment of the likelihood that pesticide exposure caused or contributed to the reported symptoms. Cases are considered to be associated with exposure to a pesticide as follows: they are evaluated as "definite" (both physical and medical evidence support exposure and consequent health effects), "probable" (incomplete or circumstantial evidence supports a relationship to pesticide exposure) or "possible" (available evidence neither supports nor contradicts a relationship). When the weight of evidence is against pesticide contribution to health effects, scientists may classify cases as "unlikely," "indirect," "asymptomatic," or "unrelated." They also have the option of declining to classify cases that lack critical information.

PISP defines an "episode" as an incident in which one or more people experience pesticide exposure from a particular source with subsequent development or exacerbation of symptoms. Occasionally, a single episode gives rise to a large number of cases.

Figure 4 summarizes numbers of chloropicrin-associated cases and episodes reported annually. The two largest chloropicrin-related episodes occurred in Kern County in 2003 and in Monterey County in 2005. The 2003 Kern County episode resulted in 165 illness reports (O'Malley *et al*., 2004a; DPR, 2005b). In this incident, 100% chloropicrin was applied over two days to fallow land near a residential area, with a buffer zone of about 18 m; the chloropicrin was injected about 0.4 – 0.5 m into the soil. Applicators dragged a weighted board behind the tractor in an attempt to confine the fumigant without compacting the soil excessively. Each of the two evenings, nearby residents complained about eye and throat irritation, although the source of the irritation was not located until the second evening. Firefighters responding to the complaints also experienced eye irritation. The irritation ceased after the soil was compacted a second time.

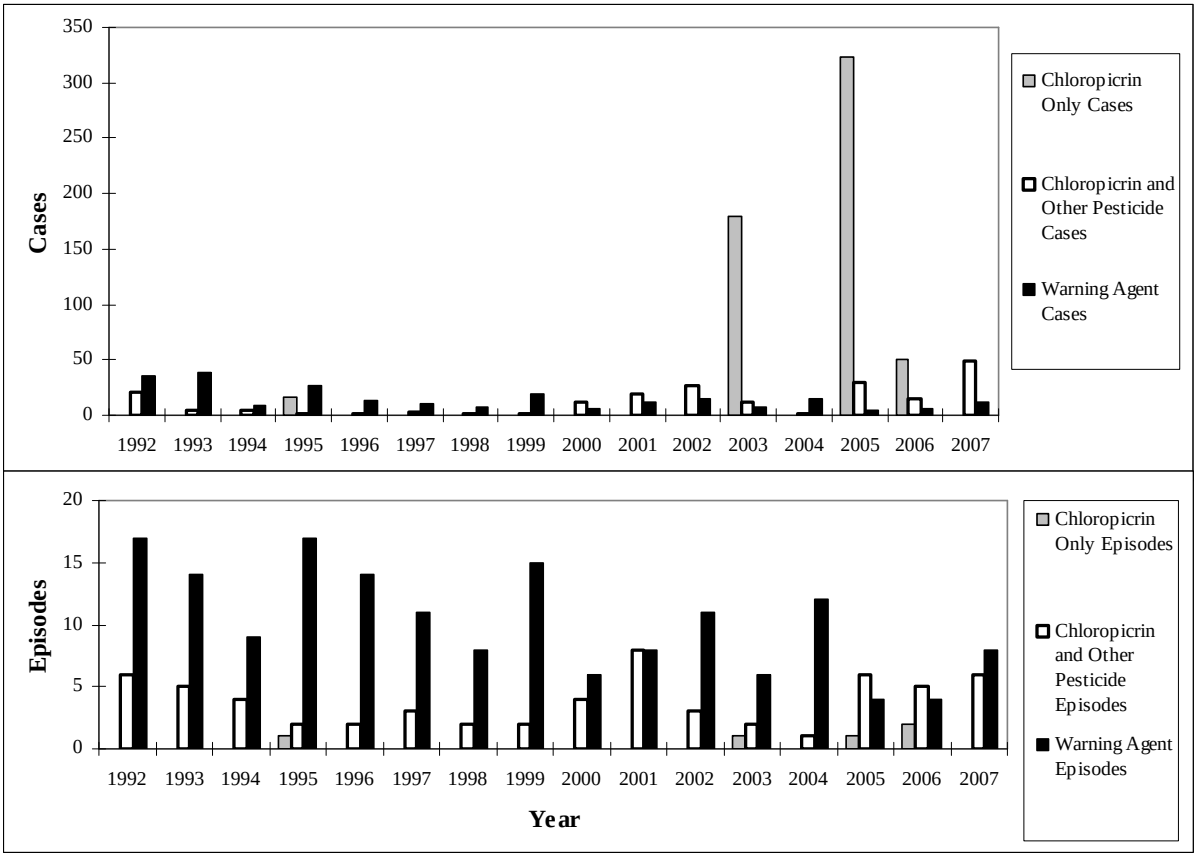
The 2005 Monterey County episode resulted in 324 cases (WHS, 2007). In this episode, following a tarped bedded application of a 94% chloropicrin product through a drip irrigation system, the system was flushed by an apparently inadequate amount of water. In the evening, residents living near the application, and up to 2 or 3 miles away, complained of odor and eye irritation.

From 1992 through 2007, PISP identified chloropicrin as the sole implicated pesticide in six California episodes involving 571 people and as one of two or more fumigants that may have contributed to another 61 episodes that gave rise to 204 cases (Mehler, 2009). All of these episodes involved agricultural soil fumigations. The fumigant combinations included three episodes (13 cases) involving the product Methyl Bromide 89.5%, which contains chloropicrin 10.5% as a warning agent. Because the chloropicrin concentration in this product is >2%, illnesses associated with this product are considered to be potentially associated with chloropicrin for illness investigation and tracking purposes. This is consistent

with U.S. EPA's designation of products containing more than 2% chloropicrin as Restricted Use Pesticides (40 CFR 152.175).

Exposure to chloropicrin used only as a warning agent was identified in 164 episodes that gave rise to 230 cases. Chloropicrin's function was not identified unequivocally in ten cases, each a separate episode; based on their circumstances, these cases were presumed to relate to warning agent use. Of these 240 cases, 57 involved agricultural use. All but seven of the other 183 cases related to structural fumigations. The seven cases involved (non-agricultural) commodity fumigations and transportation of used pesticide containers.

Figure 4. Numbers of Illnesses (Cases) and Episodes Reported in California, 1992 – 2007, Evaluated by the California Pesticide Illness Surveillance Program as Definitely, Probably, or Possibly Related [a] to Chloropicrin Exposure or That Were Associated with or Indirectly Related to Fumigants with Chloropicrin as a Warning Agent



[a] "Definite" means that both physical and medical evidence document exposure and consequent health effects, "probable" means that limited or circumstantial evidence supports a relationship to pesticide exposure, and "possible" means that evidence neither supports nor contradicts a relationship (Mehler, 2009). More than one case can be associated with each episode.

Of the 571 people exposed to chloropicrin alone, 557 (including four applicators) experienced airborne exposure and 14 entered chloropicrin-contaminated areas after the application concluded. The 155 people exposed to chloropicrin combined with other fumigants included 22 applicators and two people ("mechanics") working on pesticide-contaminated equipment. Eight of the pesticide handlers had direct contact with the fumigants. One "mechanic" and 44 applicators were among the 228 people exposed to chloropicrin used as a warning agent with other fumigants. All the other exposed people were essentially bystanders, including some who acted in a professional capacity (emergency responders, agricultural investigators), and some who traveled through the affected area in vehicles.

Table 4 summarizes the types of illnesses attributed to chloropicrin, to other fumigants used with chloropicrin, or evaluated as indirectly related to fumigant exposure. An indirect relationship indicates that protective measures required by pesticide regulations or a pesticide product label, rather than pesticide exposure, caused or contributed to health effects. (An example of an indirect relationship would be heat stress caused by wearing chemical resistant clothing while handling a pesticide for which such clothing is required.) When used as a warning agent, chloropicrin is considered a protective measure relative to the fumigants with which it is used. Table 4 suggests the prominence of eye effects among people exposed to chloropicrin. Figure 5 further clarifies the relationship between chloropicrin concentration and prevalence of eye effects.

Of the 1,015 cases summarized in Table 4, 560 reported symptoms from more than one of the coded categories (eye, skin, respiratory, and systemic). Figure 5 summarizes the percentage of cases reporting each symptom type. The dominance of eye effects is especially notable in illnesses associated with chloropicrin alone. Eye effects, including irritation, burning, itching and watery eyes, were reported in 804 (79%) of all cases, but in 547 of 571 (96%) of chloropicrin-only cases. In contrast, eye effects were reported in just 146 of 204 (72%) cases associated with chloropicrin in combination with other fumigants, and only 111 of 240 (46%) cases associated with chloropicrin as a warning agent reported eye effects.

Reports of skin and systemic illnesses demonstrate the opposite trend. Of the 571 cases associated with chloropicrin alone, 6 (1%) reported skin effects; of the 204 cases associated with chloropicrin in combination with other fumigants, 14 (7%) reported skin effects; and of the 240 warning agent cases, skin effects were reported in 55, or 23%. Systemic effects were reported in 32% of cases associated with chloropicrin alone, 41% of the cases associated with chloropicrin in combination with other fumigants, and 64% of the warning agent cases. No clear trend was apparent for respiratory manifestations, which are recognized effects both of chloropicrin and of other fumigants.

Table 4. Types of Illness Cases Reported in California That Were Potentially Associated with Chloropicrin Exposure or That Were Associated with or Indirectly Related to Fumigants with Chloropicrin as a Warning Agent (1992-2007) [a]

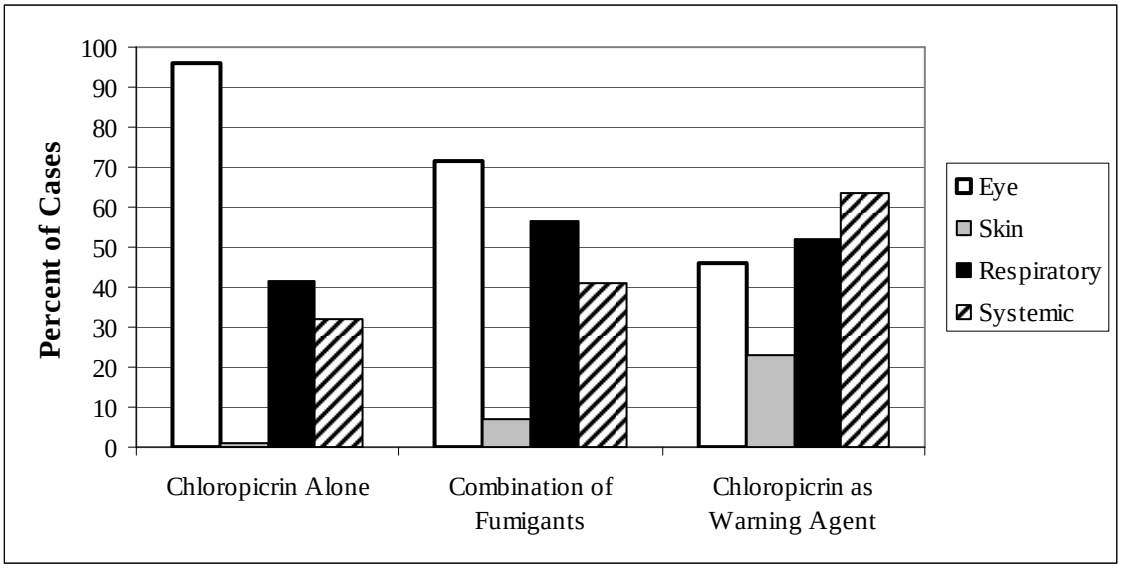
Illness Type [b]	Alone [c]	In Combination [d]	As Warning Agent [e]	Total
Eye only	246	49	19	314
Eye & Respiratory	126	46	21	193
Eye, Respiratory & Systemic	94	29	34	157
Eye & Systemic	75	16	15	106
Systemic	10	16	44	70
Respiratory & Systemic	4	19	36	59
Respiratory	10	16	16	42
Skin	0	4	25	29
Other combinations of types [f]	6	9	30	45
Total	571	204	240	1,015

[a] "Definite" means that both physical and medical evidence document exposure and consequent health effects, "probable" means that limited or circumstantial evidence supports a relationship to pesticide exposure, and "possible" means that evidence neither supports nor contradicts a relationship (Mehler, 2009).
[b] Eye effects include irritation, burning, itching and watery eyes. Respiratory illnesses include irritation of nose, throat, and lungs; coughing; wheezing; lung congestion; asthma and other breathing difficulties. Systemic illnesses include symptoms such as nausea, dizziness, headache, numbness. Skin effects include itching, rashes, and burns.
[c] Chloropicrin was applied as a sole active ingredient.
[d] Chloropicrin formulated in a product with 1,3-dischloropropene or methyl bromide in which the chloropicrin concentration is above 2%. Includes thirteen cases involving Methyl Bromide 89.5%, which contains chloropicrin 10.5% as a warning agent. Of these thirteen cases, seven reported effects to eyes along with respiratory illness, four reported only eye effects, one reported only skin effects, and one reported eye effects and systemic illness (see footnote *b* for explanation).
[e] Chloropicrin used in conjunction with sulfuryl fluoride, or formulated with methyl bromide in a product with chloropicrin concentration less than or equal to 2%.
[f] Includes seven less commonly reported combinations of eye, skin, respiratory, and systemic effects.

Illnesses Reported in Open Literature

Additional incidents reported in California are described in the literature (Goldman *et al*., 1987; Prudhomme *et al.*, 1999). Goldman *et al*. (1987) describe a complaint of illness following "off-gassing" of chloropicrin and methyl bromide from an episode occurring in 1984. In the introduction, four episodes the authors called "community exposures" are briefly described. The episodes occurred in Los Angeles County (1973; 3 cases), Ventura County (1980; 16 cases), Kern County (1984; 3 families affected), and Stanislaus County (1984; 32 cases). The fourth incident resulted in evacuation of 75 homes and three businesses, and 31 persons reported symptoms consistent with chloropicrin exposure (eye, nose, or throat irritation; noticing an unusual odor).

Figure 5. Percent of Illnesses (Cases) Reporting Eye, Skin, Respiratory, and Systemic Symptoms in California, 1992 – 2007, Evaluated by the California Pesticide Illness Surveillance Program as Definitely, Probably, or Possibly Related [a] to Chloropicrin Exposure, Alone or in Combination with Another Fumigant, or That Were Associated with or Indirectly Related to Fumigants with Chloropicrin as a Warning Agent



[a] "Definite" means that both physical and medical evidence document exposure and consequent health effects, "probable" means that limited or circumstantial evidence supports a relationship to pesticide exposure, and "possible" means that evidence neither supports nor contradicts a relationship (Mehler, 2009). More than one type of symptom can be reported in each case.

Prudhomme *et al.* (1999) described respiratory damage to three men exposed in a 1995 episode to chloropicrin vapor in a truck trailer at a freight transportation company. Six weeks later, the men were seen at a clinic in San Francisco for follow-up of their persistent chest-wall pain, and were found to have elevated creatine phosphokinase levels, suggesting damage to skeletal muscle. The reason for the elevated creatine phosphokinase levels was unknown; although earlier reports suggested that violent coughing could cause that sort of muscle damage, coughing was not a prevalent symptom of the exposed employees.

Chloropicrin concentrations during episodes are rarely reported, and exposures of persons reporting illnesses are almost never known. One exception is reported in a follow-up to an episode, which occurred in Minnesota, where chloropicrin was released into the basement of an empty home to (illegally) fumigate for bats (Teslaa *et al.*, 1986). Three or four weeks later, a family moved into the house. A week after moving in, family members reported runny noses, lacrimation, and coughing. A family dog kept in the basement at night developed pneumonia. Six weeks after the chloropicrin application to the basement, air and cloth samples taken inside the house (upstairs, not in the basement) showed chloropicrin at concentrations of 30 - 48 ppb (202 - 323 $\mu g/m^3$) on the ground floor, and 3 ppb (20 $\mu g/m^3$) in an upstairs bedroom.

O'Malley *et al*. (2004a) used standard air-dispersion modeling to estimate 1-hour average chloropicrin air concentrations in areas south and west of the treated Kern County field during the 2003 episode. These estimates were as high as 200 ppb (1,340 $\mu g/m^3$). Similar techniques were applied to the Monterey episode (Barry and Marade, 2007), for which modeling also predicted 1-hour time-weighted average air levels in the range of 50 to 200 ppb (336 – 1,340 $\mu g/m^3$), with 3-minute concentrations as high as 800 ppb (5,380 $\mu g/m^3$).

LABEL PRECAUTIONS AND CALIFORNIA REQUIREMENTS

Label Precautions

Chloropicrin products are all Toxicity Category I pesticides and have the signal word DANGER (or DANGER POISON, with skull and crossbones) on the label. Due to acute inhalation toxicity, all products containing more than 2% chloropicrin are classified as RUPs according to U.S. EPA (40 CFR 152.175). Chloropicrin is listed as a Restricted Material under California regulations (3 CCR 6400). As a Restricted Material in California, chloropicrin may only be applied by, or under the supervision of, a certified applicator. The operator of the property must first obtain a permit from the County Agricultural Commissioner. Permit conditions may be required by the County Agricultural Commissioner.

Chloropicrin is available in 100% formulations, or it can be formulated with methyl bromide or 1,3-dichloropropene. Products containing methyl bromide or 1,3-dichloropropene have warning statements for these AIs. Typical precautionary statements for a product label (100% chloropicrin) are as follows: "DANGER. Poisonous liquid and vapor. Inhalation of vapors may be fatal. Chloropicrin is readily identifiable by smell. Exposure to very low concentrations of vapor will cause irritation of eyes, nose, and throat. Continued exposure after irritation, or higher concentrations may cause painful irritation to the eyes or temporary blindness. Liquid will cause chemical burns to skin or eyes. Do not get on skin, in eyes, or on clothing. Harmful or fatal if swallowed."

California Requirements

Under California regulation, field soil fumigation with chloropicrin and methyl bromide (excepting golf courses, tree holes, potting soil, raised-tarpaulin nursery fumigations of less than one acre (0.405 ha), and greenhouses and other similar structures) is regulated under 3 CCR 6447 – 6447.3 and 3 CCR 6780 – 6784. These regulations impose requirements for tarp use (if tarps are to be used) and limit the size of application blocks to 40 acres (16 ha; 3 CCR 6447(d)). These regulations do not apply to soil fumigations done with chloropicrin only (i.e., without methyl bromide).

California regulation places additional restrictions on fumigation of nursery potting soils or soil mixes, nursery stock, and other agricultural commodities, appliances, or equipment, with either chloropicrin or methyl bromide (or any mixture of the two chemicals) under 3 CCR 6453. This regulation specifies that fumigations of these types must be done in either "a

properly sealed fumigation chamber, railroad car, or truck trailer, or under a gas confining tarp approved by the commissioner or director."

Structural fumigations with mixtures of methyl bromide and chloropicrin are regulated under 3 CCR 6454. These regulations require that chloropicrin be used as a warning agent whenever methyl bromide is used to fumigate a structure, unless prohibited by other regulations or by product labeling (the chloropicrin concentration is not specified). These regulations further specify requirements for tarps, buffer zones, and aeration based on application rates of methyl bromide.

In January 2008, California finalized regulations to control emissions of volatile organic compounds in certain parts of the state. Regulations for chloropicrin limit the application methods that are allowed in certain parts of the state at certain times of the year, and cap the allowed application rate to 400 lbs AI/acre (449 kg/ha; 3 CCR 6449 – 6449.1). As these restrictions do not apply to all areas of the state and all times of the year, they are not incorporated into exposure estimates reported in this exposure assessment.

EXPOSURE SCENARIOS

An exposure scenario describes a situation where people may contact pesticides or pesticide residues, and in which the nature of the exposure as well as its magnitude (apart from variability among individuals and occasions) is relatively homogeneous. To facilitate review of whether chloropicrin meets the criteria to be listed as a Toxic Air Contaminant, this exposure assessment focuses on airborne exposures to bystanders adjacent to pesticide application, in indoor air, and in ambient air.

Screening estimates are provided in this exposure assessment. Although individuals in each scenario might potentially be exposed to a range of chloropicrin concentrations, for quantitative risk assessment purposes the highest realistic exposures, based on available data, are determined; if these estimates result in acceptable risk, then lower exposures will, as well. Screening estimates are calculated using the maximum application rate allowed in California, along with any other conditions that would tend to increase exposure. Ideally, screening estimates provide the maximum realistic exposure. To achieve their purpose it is critical that estimates do not underestimate actual exposures.

Bystanders

Bystanders include individuals, working or not, who are not directly involved with a pesticide application but who may be exposed to airborne pesticide during or after the application, by drift or volatilized pesticide. Exposure scenarios include bystanders to a soil fumigation, to a structural fumigation, and to an enclosed space fumigation. All three of these types of fumigations can use chloropicrin as a warning agent. Additionally, both soil and space fumigations can use chloropicrin at higher rates as an AI, and screening estimates for these scenarios assume chloropicrin as an AI. As chloropicrin is used only as a warning agent in

structural fumigations, screening exposure estimates assume chloropicrin is used as a warning agent.

Bystanders are assumed to wear no protective clothing or equipment, as is required for handlers of chloropicrin-containing products during an application. Occupational bystanders may be handling other pesticides or they may be doing fieldwork such as harvesting, and are assumed to be present next to the chloropicrin application for an 8-hour workday. Residential bystanders are assumed to be in the vicinity of the chloropicrin application for 24-hour days.

Indoor Air

The California Health and Safety Code Section 39660.5 requires that TAC assessments consider indoor air concentrations as well as ambient outdoor air. Members of the public can potentially be exposed to chloropicrin in indoor air if they enter a structure following fumigation.

Ambient Air

Air monitoring done in California (ARB, 2003a; 2003b) suggests that airborne exposures to chloropicrin are possible even in areas that are far from application sites. Ambient air monitoring was conducted by the California Air Resources Board (ARB) in three counties with relatively high chloropicrin use (Kern, Monterey, and Santa Cruz), during times when peak use was anticipated.

PHARMACOKINETICS

Dermal and Inhalation Absorption

Dermal Absorption

Critical toxic effects from exposure to chloropicrin vapor are primarily due to contact with eyes and respiratory tract, causing irritation (OEHHA, 1999; OEHHA, 2001; U.S. EPA, 2008). For chemicals such as chloropicrin where the primary toxic effect is localized irritation, the effect is related to concentration in air rather than absorbed dose (Pauluhn, 2003). As exposure estimates are appropriately reported as concentrations rather than as absorbed doses, no dermal absorption estimate is required.

Inhalation Absorption

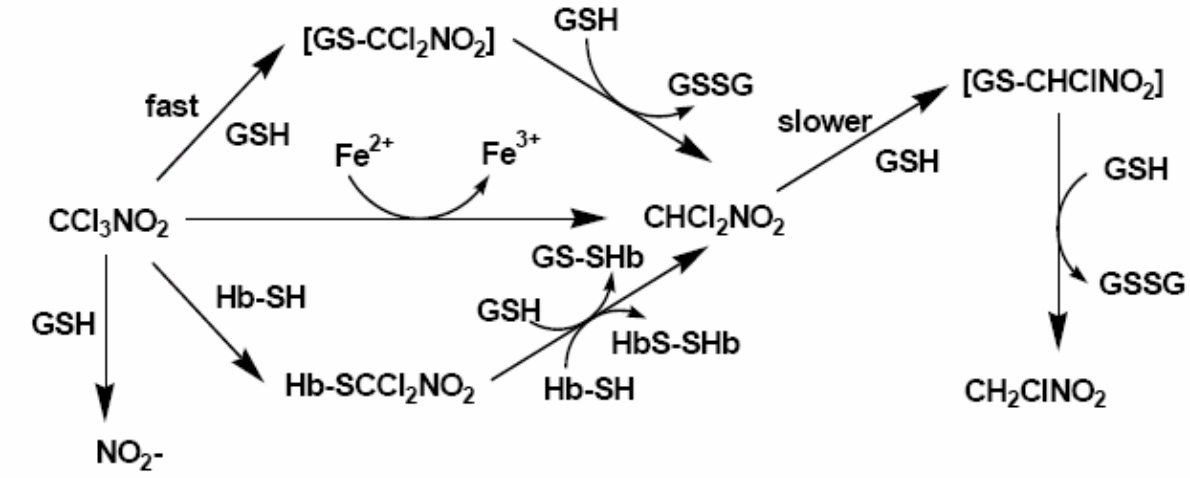
Critical toxic effects from exposure to chloropicrin vapor are primarily due to contact with eyes and respiratory tract, causing irritation (OEHHA, 1999; OEHHA, 2001; U.S. EPA, 2008). For chemicals such as chloropicrin where the primary toxic effect is localized irritation, the effect is related to concentration in air rather than absorbed dose (Pauluhn, 2003). As exposure estimates are appropriately reported as concentrations rather than as absorbed doses, no inhalation absorption estimate is required.

Metabolism

Limited data are available on the metabolism of chloropicrin. Metabolism in mammals was investigated in only two *in vivo* studies, both using male albino Swiss-Webster mice weighing 20 – 25 g (Sparks *et al.*, 1997; Sparks *et al.*, 2000). Both studies also included *in vitro* components to investigate specific reactions, which will be briefly discussed below following discussion of the *in vivo* data. Together, these studies suggest that most absorbed chloropicrin is eliminated through urine, and that the chief metabolic pathway for chloropicrin is through dechlorination reactions with biological thiols, followed by formation of multiple metabolites which are mostly excreted in urine. Figure 6 summarizes the metabolic pathways proposed by Sparks *et al.* (1997).

Alwis *et al.* (2008) developed an analytical method for quantifying nitromethane in human blood as a potential biomarker for exposure to chloropicrin. In a series of in vitro studies, blood samples spiked with chloropicrin were extracted with solid-phase microextraction and quantitated by gas chromatography/high resolution mass spectrometry. Nitromethane was the major product formed by reactions in the blood samples; it formed gradually over a 48-hour interval. Dichloronitromethane and chloronitromethane also were detected. No pathway was proposed for the reactions. Alwis *et al.* (2008) also found variable background nitromethane in blood drawn from individuals with no known exposure to either nitromethane or chloropicrin.

Figure 6. Proposed pathways for reaction of chloropicrin with glutathione and hemoglobin [a]



[a] Sparks *et al.* (1997)

In Vivo Studies

Sparks *et al.* (1997) administered ^{14}C-radiolabeled chloropicrin in a triethylene glycol vehicle, both orally (two mice) and via intraperitoneal injection (four mice), at doses in the range of 1-3 mg/kg. Of the four mice treated intraperitoneally, two were euthanized at one hour and two

at 48 hours post-dose. Both orally-dosed mice were euthanized 48 hours post-dose. Most of the administered radiolabel was recovered from urine, feces, and expired gases; the total eliminated by these routes averaged 81% following the intraperitoneal dose and 65% of the oral dose. In mice dosed by either route, about 43-47% of the radiolabel was recovered in urine excreted during the first 24 hours post-dose; an additional 8% was recovered from urine excreted between 24 and 48 hours post-dose. Another 2.5 – 13% was recovered from feces through 48 hours post-dose, and 0 – 15% was recovered from expired gases. The radiolabeled compounds recovered after dosing were not identified, though thin-layer chromatography showed that some compounds recovered from urine were polar.

Sparks *et al*. (2000) administered non-radiolabeled chloropicrin in a dimethylsulfoxide vehicle via intraperitoneal injection to four mice at a dosage of 5 mg/kg. All four mice were euthanized at 24 hours post-dose. Urine collected from the mice during that interval was assayed for 2-thioxothiazolidine-4-carboxylic acid (also called, "raphanusamic acid"). This metabolite, a cyclic cysteine adduct with thiophosgene ($CSCl_2$), was detected in an amount equivalent to about 1% of the administered chloropicrin dose. Excretion of this metabolite suggests that at least one metabolic pathway for chloropicrin proceeds via formation of thiophosgene intermediates.

Interactions of chloropicrin with blood proteins were investigated in groups of three mice intraperitoneally injected with doses of 5, 14, 25, and 50 mg/kg chloropicrin (Sparks *et al*., 2000). Mice were euthanized 1 hour post-dose. Blood samples were collected from each mouse using cardiac puncture, and the liver was removed, rinsed with phosphate buffer, homogenized, and centrifuged to yield cytosolic samples for assay. Assays conducted on liver cytosol samples included total hemoglobin, oxyhemoglobin, and hemoprotein levels. All three assays showed dose-dependent increases, suggesting that chloropicrin interacts with these proteins in the liver during the first hour post-dose. Whole blood samples were lysed with deionized water and assayed for percent methemoglobin. Percent methemoglobin ranged 0-3, suggesting that chloropicrin and its metabolites did not substantially produce methemoglobin, at least within an hour after dosing.

In Vitro Studies

When mixed in a phosphate buffer with each of several biological thiols (including glutathione, cysteine, N-acetylcysteine, coenzyme A, and reduced lipoic acid), chloropicrin reacted rapidly (Sparks *et al*., 1997). These reactions resulted in both the dechlorination of chloropicrin to dichloronitromethane, and production of the disulfide of each thiol. Chloropicrin reacted completely when mixed in a phosphate buffer with two proteins containing free thiols, hemoglobin (from dog and human) and alcohol dehydrogenase (from yeast), forming both dichloronitromethane and protein adducts. In contrast, a protein with no sulfhydryl group (myoglobin) and one with partially blocked sulfhydryl groups (albumin), did not take up the radiolabel when mixed in a phosphate buffer with chloropicrin (Sparks *et al*., 1997). These data suggest that chloropicrin could be anticipated to react most readily with free thiols and thiol proteins.

In one of four *in vitro* studies to investigate reactions potentially resulting in mammalian toxicity, chloropicrin was incubated in a phosphate buffer with either pyruvate dehydrogenase (30 minutes) or succinate dehydrogenase (5 minutes). Following the incubation period, the enzyme activity was assayed for each of these thiol proteins; chloropicrin was a potent inhibitor of both (Sparks *et al*., 2000). These data further confirm the reactivity of chloropicrin with thiol proteins. Sparks *et al*. (2000) suggested a metabolic pathway that proceeds to either phosgene or raphanusamic acid. Phosgene was proposed to be formed via two pathways, with intermediates thiophosgene and trichloromethanol. Formation of phosgene, via a trichloromethanol intermediate that spontaneously dechlorinates, has been established as a major metabolic pathway for chloroform (Mansuy *et al.*, 1977; Meek *et al*., 2002), providing support for the pathway suggested by Sparks *et al*. (2000). However, it is unclear whether this is the dominant pathway for chloropicrin, as it is for chloroform.

ENVIRONMENTAL CONCENTRATIONS

Air

In California, chloropicrin concentrations have been monitored in the air surrounding application sites and in ambient air away from individual applications but during peak application season. These studies are discussed below.

Ambient Air

Chloropicrin concentrations have been monitored by ARB in ambient air, not associated with specific applications. Samplers in each case consisted of duplicate sampling tubes containing XAD-4 resin. Information about all three studies is summarized in Table 5, including reported detection and quantification limits and the maximum concentration reported in each study. The limit of detection (LOD), also called the method detection limit, is "...the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero..." (Segawa, 1995). The limit of quantification (LOQ), sometimes called the "estimated quantitation limit," is a threshold above which results are generally considered reliable (Helsel, 2005).

Ambient air monitoring was conducted by ARB in an area and at a time when chloropicrin was anticipated to be high. However, actual locations and timing of applications can vary relative to monitoring, and although general information about applications in an area is available through the PUR, applications are reported in the PUR in 1-mi^2 sections and distances of applications from ambient air samplers are unknown. Furthermore, applications spanning multiple days in a single field can be reported in PUR as occurring on a single date; thus, there is no way to exactly relate applications to ambient air monitoring data. However, examination of Table 5 suggests that the reported concentrations may underestimate actual ambient air concentrations for short-term exposures. For example, the earliest ambient air study (ARB, 1987) was unable to detect chloropicrin in most samples. Monitoring conducted in 2000 was limited, with just five samplers and samples collected for 72 hours in association with two nearby soil fumigations with methyl bromide/chloropicrin products. Chloropicrin

was not detected in any of the 60 samples; method detection limits were 0.111 μg/m^3 for 8-hour samples and 0.056 μg/m^3 for 16-hour samples. Of the two studies done in 2001, the one in Kern County reported mostly non-detects; just five of 198 samples contained chloropicrin above the LOQ (ARB, 2003a). And in the other study conducted in 2001, 149 of 192 samples contained chloropicrin above the LOQ; this study also reported the highest 24-hour chloropicrin concentration measured in ambient air not adjacent to an application, 14.3 μg/m^3 (ARB, 2003b).

Table 5. Ambient Air Monitoring for Chloropicrin in California Counties Conducted by the Air Resources Board (ARB)

County	Dates	No. Samples	LOD [a] (μg/sample)	LOQ [b] (μg/sample)	Samples ≥ LOQ	Maximum (μg/m^3) [c]
Monterey [d]	8/26/86 – 9/18/86	96	0.085	0.425	4	4.56
Santa Barbara [e]	10/7/00 – 11/19/00	60	0.016	0.200	0	Not detected
Kern [f]	6/30/01 – 8/31/01	198	0.00396	0.0198	5	0.75
Monterey, Santa Cruz [g]	9/08/01 – 11/8/01	192	0.00396	0.0198	149	14.0

[a] Limit of Detection. In some study reports, this is called the "method detection limit," or MDL. It was set in the three most recent studies as 3.14 x the standard deviation following analysis of seven replicate cartridges spiked at a level near the anticipated LOD (ARB, 2003a; ARB, 2003b; Wofford *et al.*, 2003). ARB (1987) did not describe the method used to determine the LOD.

[b] Limit of Quantification. In some study reports, this is called the "estimated quantitation limit," or EQL. It is set as 5 times the LOD. ARB (1987) did not report the LOQ; the one reported here was calculated by multiplying the LOD by 5. Wofford *et al.* (2003) did not specify how the LOQ was determined, other than to say it was the level above which results could be quantitated, and that it was rounded to 0.2 μg/tube.

[c] Multiply value by 0.1487 to get result in parts per billion (ppb).

[d] ARB (1987). Three sites plus background. Samples were each collected over 4 hours. Sample sites and dates were selected to coincide with preplant applications for strawberries. Results above the LOD were reported by ARB (1987), including 20 of 96 samples.

[e] Wofford *et al.* (2003). Five sites in the city of Lompoc. Samples were collected in 8- to 16-hour intervals for a total of 72 hours beginning with each of two nearby soil fumigations. No chloropicrin was detected in any sample; the LODs for 8- and 16-hour samples were 0.111 and 0.056 μg/m^3, respectively.

[f] ARB (2003a). Four sites plus background. Samples were each collected over 24 hours. Sample sites and dates were selected to coincide with preplant applications for carrots.

[g] ARB (2003b). Four sites in Monterey County (including one background site) and two sites in Santa Cruz County; three of the six sites did not have strawberry fields within a 3-mile radius, while the other three sites had strawberry fields within 360 feet to 1 mile. Samples were each collected over 24 hours. Sample sites and dates were selected to coincide with preplant applications for strawberries.

Chloropicrin concentrations reported in these ambient air monitoring studies are lower than those reported during application site monitoring (see the next section). This is consistent with studies showing that the highest airborne pesticide concentrations occur adjacent to an application (MacCollom *et al.*, 1968; Siebers *et al.*, 2003). As insufficient information is available to determine how concentrations measured in ambient air monitoring relate to the range of concentrations actually encountered by the public, and to assure health-protective estimates, concentrations reported in ambient air monitoring were not used to estimate airborne chloropicrin exposures.

Application Site Air – Soil Fumigation

Two types of data have been collected during air monitoring associated with chloropicrin applications: air concentration samples taken on-site for direct estimation of chloropicrin field volatility (emission rate or flux), and off-site concentrations of chloropicrin in air. Results are reported as time-weighted average (TWA) concentrations.

Off-site concentrations are reported below. Measured air concentrations can fluctuate throughout a sampling interval, with the environmental conditions that affect measured air concentrations being specific to a particular application. Measurements taken during one particular application cannot be directly generalized to applications occurring under different environmental conditions (Johnson *et al*., 1999). Consequently, it is unlikely that the measurements from one particular study will capture the highest possible air concentrations for an application method.

Field volatility data for chloropicrin, and concentration estimates based on these data, are summarized following the discussion of measured off-site concentrations. Flux, or emission rate, is the rate at which a chemical's mass moves out of the ground into the air, and is expressed in this document with units of $\mu g/m^2/sec$. Direct estimation of flux uses air concentrations measured by multiple samplers attached at different heights to a sampling mast in the center of the field. Regression of the logarithm of sampler height against the wind speed, air temperature, and TWA concentrations at each height yields the flux estimate for each time interval; an example of this type of calculation was provided by Majewski *et al.* (1990). All chloropicrin flux estimates reported in this exposure assessment were obtained by using direct flux estimation.

Flux data are used, together with an appropriate air dispersion model, to estimate off-site concentrations associated with a fumigation. Air dispersion models use mathematical equations to simulate how air molecules, and volatilized chemicals mixed with them, move away from the chemicals' source (a fumigated field in this case). DPR uses the Industrial Source Complex Short Term model, Version 3 (ISCST3), to estimate off-site concentrations. ISCST3 is based on a steady-state Gaussian plume dispersion equation, which means that the chemical is assumed to have a normal (or Gaussian) distribution of concentrations within the plume, with the concentration peak occurring at the plume's centerline and concentrations decreasing along the edges of the plume. The model is "steady-state" in that TWA concentrations are calculated assuming constant emission rate and meteorological conditions for each hour; conditions may vary from one hour to the next (U.S. EPA, 1995). ISCST3 assumes that off-site concentrations are proportional to flux. DPR analysis imposes the additional assumption that flux is proportional to application rate (Johnson *et al.*, 1999).

Chloropicrin concentrations were modeled using the "screening" mode in ISCST3. As explained by Barry (2008a), "screening mode produces a single air concentration estimate at a receptor (a point location at a specified distance from the source) using a single set of worst-case meteorological conditions. This means that a single downwind centerline set of air concentration estimates at various distances is the result of the analysis." Barry (2008a)

mentions other ISCST3 modes, which use historical meteorological data "to produce multiple air concentration estimates at each receptor. This produces a distribution of air concentrations at a given receptor over the span of the meteorological data." In the screening mode, DPR first simulates generic downwind centerline concentrations using a default flux of 100 $\mu g/m^2/sec$. Next, the generic downwind centerline concentrations are adjusted for the flux estimated during the study, and for application rate. The adjusted concentrations are used to estimate bystander exposures.

Off-Site Concentrations

Preliminary monitoring studies of off-site concentrations in air of methyl bromide and chloropicrin were conducted by DPR during three shallow shank tarped broadcast applications in 1982 and 1983 in Orange County (Maddy *et al.*, 1983; 1984). Neither the application rate of the methyl bromide/chloropicrin mixture nor the proportion of chloropicrin in the mixture was reported, precluding the use of these data in estimating exposure. Maximum chloropicrin concentrations reported were 713 $\mu g/m^3$ (106 ppb) at 25 ft (7.6 m) downwind and 545 $\mu g/m^3$ (81 ppb) at 50 ft (15 m) downwind.

Monitoring of off-site chloropicrin concentrations in conjunction with soil fumigations has been conducted by ARB (1987; 2003c; 2004; 2006) as well as in studies submitted by registrants (Beard *et al.*, 1996; Rotondaro, 2004). With the exception of ARB (1987), these data sets are summarized in Table 6, and briefly described below. ARB (1987) monitored off-site concentrations during a 2-day tarped broadcast application to a strawberry field of an unspecified methyl bromide/chloropicrin mixture using three samplers, one 902 ft (275 m) NW of the field, and two 220 ft (67 m) and 574 ft (175 m) SE of the field. No information was reported about the field size or the application rate, precluding the use of these data in estimating bystander exposure. The maximum chloropicrin concentration reported in this study was 160 $\mu g/m^3$ (24 ppb) during a 3-hour sample collected on the second application day at the sampler located 574 ft (175 m) SE of the field edge.

In 2007, the California Rural Legal Assistance (CRLA) commissioned air monitoring near a tarped shallow shank broadcast fumigation in August 2007 in Monterey County (CRLA, 2008). 12-hour samples were collected over two 4-day sampling periods, using samplers with XAD-4 tubes placed outside two homes. A mixture containing methyl bromide and chloropicrin was applied during the first sampling interval, in field blocks approximately 250 and 1,200 ft (76 and 366 m) from the two samplers, and a mixture of 1,3-dichloropropene and chloropicrin was applied during the second monitoring interval, approximately 140 and 185 ft (43 and 56 m) from the samplers. Chloropicrin application rates were reported to be 190 lbs/acre (213 kg/ha) in each application. Due to a high flow rate of 1 liter per minute during the first 4-day sampling interval, breakthrough occurred (i.e., failure of sampler tubes to completely retain sorbed chloropicrin), and a 500-ng field spike had 64% recovery compared to an average of 107% for lab spikes. The flow rate was correctly set at 0.1 liters per minute during the second 4-day sampling interval, and no breakthrough occurred. Chloropicrin concentrations in samples not affected by breakthrough ranged 1.6 - 40 $\mu g/m^3$ (0.23 – 5.9 ppb).

Table 6. Studies Monitoring Off-Site Chloropicrin Concentrations During and Following Soil Fumigation Applications

Application Method	Rate (lbs AI/acre) [a]	Sampler Distance (m) [b]	Total Samples	LOQ [c] (µg/sample)	Samples ≥ LOQ	Maximum Concentration ($\mu g/m^3$) [d]	Maximum Concentration (hours) [e]
Broadcast non-tarped [f]	171	18 – 55	398	0.07	209	1,820	6.52
Broadcast tarped [f]	332	18 – 55	444	0.07	242	968	6.00
Broadcast tarped [g]	343	18 – 55	444	0.07	438	677	6.00
Broadcast tarped [h]	346	18 – 55	444	0.07	243	868	13.0
Bedded non-tarped [f]	86	18 – 55	264	0.07	106	1,760	6.00
Bedded tarped [i]	125	265	64	0.150	22	39	14.8
Bedded tarped [j]	150	50	44	0.0198	43	270 [k]	10.6
Bedded tarped [f]	189	18 – 55	420	0.07	196	1,810	6.10
Bedded tarped drip [l]	188	20	62	0.0198	62	415	8.4
Bedded tarped drip [m]	156	15	255	0.1	81	349	3.82
Greenhouse drip [n]	13.6	1.5	224	0.1	4	14.9	5.58
Greenhouse drip [n]	166	1.5	256	0.1	203	577	4.00
Greenhouse drip [n]	174	1.5	224	0.1	30	108	4.02

[a] For bedded applications, the reported rate is for the total acres, including furrows as well as beds. Beds reduce treated acres by 50 – 58%. Multiply value by 1.123 to get rate in kilograms per hectare (kg/ha).
[b] Sampler distance from edge of greenhouse, otherwise from edge of treated plot.
[c] LOQ: Limit of Quantification. In some study reports, this is called the "estimated quantitation limit," or EQL.
[d] Highest measured concentration associated with the application. Multiply value by 0.1487 to get result in parts per billion (ppb).
[e] Time interval for sample with highest reported concentration associated with the application (i.e., the concentration in the previous column).
[f] Fumigant consisting of 99.4% chloropicrin was applied to plots near Phoenix, Arizona (Beard *et al*., 1996).
[g] Fumigant consisting of 99.4% chloropicrin was applied to a field in Washington (Beard *et al*., 1996).
[h] Fumigant consisting of 99.1% chloropicrin was applied to a field in Florida (Beard *et al*., 1996).
[i] Fumigant consisting of 50:50 chloropicrin:methyl bromide was applied over three days at 250 lbs product/acre (125 lbs chloropicrin/acre), to a 22-acre (8.9-ha) field in Monterey County, California (ARB, 2003c).
[j] Fumigant consisting of 50:50 chloropicrin:methyl bromide was applied at 300 lbs product/acre (150 lbs chloropicrin/acre), to a 4.8-acre (1.9-ha) field in Santa Cruz County, California (ARB, 2004).
[k] This concentration occurred during background sampling. Nearby applications were documented on days preceding the monitored application.
[l] Fumigant consisting of 94% chloropicrin was applied to an 8.2-acre (3.3-ha) field in Santa Barbara County, California (ARB, 2006).
[m] Fumigant consisting of 99.1% chloropicrin was applied to a California field (Rotondaro, 2004).
[n] Fumigant consisting of 99.1% chloropicrin was applied to beds in a California greenhouse (Rotondaro, 2004).

Off-site concentrations of chloropicrin were monitored adjacent to bed fumigations by ARB in three studies conducted between 2001 and 2005 (ARB, 2003a; 2004; 2006). Two of these were associated with applications of methyl bromide/chloropicrin mixtures, and applications and monitoring were impacted by regulatory requirements for soil fumigations with methyl bromide, including buffer zone requirements. The third study (ARB, 2006) involved monitoring during and following an application of a 94% chloropicrin product. Samplers

consisted of 8 mm x 150 mm adsorbent tubes containing 400 mg XAD-4 resin, with a back-up section of 200 mg of XAD-4 resin to verify that no breakthrough occurred, connected to sampling pumps with Teflon tubing and fittings. The pump flow rate was 90 standard cubic centimeters per minute (i.e., flow rate is referenced to a standard temperature of 25°C and standard pressure of 760 mm Hg; approximately equal to 0.1 liters per minute), calibrated with a digital mass flowmeter at the start and end of each sampling interval. The sampler flow rate was increased to 100 standard cubic centimeters per minute in the second and third studies (ARB, 2004; 2006). The optimal sampler flow rate was determined during method validation; chloropicrin breakthrough occurred readily at higher flow rates, but not at 0.1 liters per minute.

Quality assurance in ARB monitoring consisted of co-located replicate sampling at one sampler; a laboratory solvent blank, a laboratory spike, a laboratory method blank and a laboratory control sample with each set of samples analyzed; trip blanks; and trip, field, and laboratory spikes. Samples were analyzed via gas chromatography with a mass selective detector operating in selective ion mode and a Restek Rtx-200 column.

In 2001, ARB monitored off-site chloropicrin concentrations during and following a shallow shank tarped bed application of a methyl bromide/chloropicrin 50:50 mixture in Monterey County (ARB, 2003c). The application was to a 22-acre (8.9-ha) field, and the application rate was 125 lbs AI/acre (140 kg/ha). Because of restrictions on the methyl bromide application, the application occurred over three days. Background samples were collected from 1500 hours on October 29 to 1000 hours on October 30; chloropicrin was detected in all of the background samples, at concentrations up to 2.0 $\mu g/m^3$ (0.3 ppb). Air monitoring around the treated field was conducted from October 31 to November 4. Eight air samplers, one on each side and one at each corner, were positioned 850 to 1,665 ft (259 to 507 m) from the field edge (two samplers were collocated on the north side of the field). The highest concentration detected was 39 $\mu g/m^3$ (5.8 ppb). Mean recovery of field spikes was 94%; sample results were not corrected for field spike recoveries.

In 2003, ARB monitored off-site chloropicrin concentrations during and following a shallow shank tarped bed application of a methyl bromide/chloropicrin 50:50 mixture in Santa Cruz County (ARB, 2004). The application was to a 4.8-acre (1.9-ha) field, and the application rate was 150 lbs AI/acre (168 kg/ha). Eight air samplers, one on each side and one at each corner, were positioned 160 ft (49 m) from the field edge (two samplers were collocated on the north side of the field). Mean recovery of field spikes was 91%. Background samples were collected from 0630 hours to 1700 hours (daytime) and 1700 hours to 0600 hours (nighttime) on November 12 to 13. Chloropicrin was above the LOQ in all of the background samples, at concentrations up to 270 $\mu g/m^3$ (40 ppb); in fact, the highest concentrations reported in the study occurred in the background samples. ARB (2004) advised caution in using results from this study because of known nearby applications, and because rain occurred during sampling, confounding interpretation of study results.

In 2005, ARB monitored off-site chloropicrin concentrations during and following a drip tarped bed application of chloropicrin 94% in Santa Barbara County (ARB, 2006). The

application was to an 8.2-acre (3.3-ha) field, and the application rate was 188 lbs AI/acre (211 kg/ha). The beds were covered with a single clear tarp, 1.34 mil thickness, with a double layer at the ends; ARB (2006) noted that the doubled tarp deviated from typical practice. Eight air samplers, one on each side and one at each corner, were positioned 60 ft (18 m) from the field edge (two samplers were collocated on the southeast corner of the field). Background samples were collected prior to the application, as usual. Chloropicrin was detected in all of the background samples, at concentrations up to 5.04 $\mu g/m^3$ (0.749 ppb); this is in the range of concentrations reported during ambient air sampling. Mean recovery of field spikes was 95%; sample results were not corrected for field spike recoveries.

In the studies conducted by Beard *et al.* (1996) and Rotondaro (2004), off-site movement of chloropicrin was monitored at sites in three states in association with soil fumigations using four different application methods. In all cases, air samples were collected with XAD-4 solid sorbent tubes having 400 mg sorbent in the front section and 200 mg in the back section; tubes were connected to pumps calibrated at 50 ml/min. Chloropicrin was analyzed by gas chromatography with a nickel-63 electron capture detector.

Beard *et al.* (1996) monitored off-site chloropicrin concentrations associated with applications to fields in Washington (broadcast tarped application), Florida (broadcast tarped application), and Arizona (broadcast tarped, broadcast non-tarped, bedded tarped, and bedded non-tarped applications). Samplers were located at 60, 120, and 180 feet (18, 37, and 55 m) from the four edges of each field (north, south, east and west). Sampling intervals were 6 hours per sample during the first 48 hours, and 12 hours per sample over the following 12 days (14 days total). The non-tarped bedded application was monitored for 7 rather than 14 days. The highest concentration during any sampling interval was 1,820 $\mu g/m^3$ (271 ppb), measured 0 – 6 hours following the non-tarped broadcast application in Arizona.

Rotondaro (2004) monitored off-site chloropicrin concentrations associated with two types of applications in California, field (outdoor) surface drip and greenhouse (indoor) surface drip. Samplers were located at a single distance, 50 feet (15 m) from the field application and 5 feet (1.5 m) from the edge of the greenhouse, at four sides and four corners of the field or greenhouse. Sampling intervals were 4 hours per sample during the first 48 hours, and 12 hours per sample for an additional 8 – 10 days (10 - 12 days total). The highest concentration from the field drip irrigation was 349 $\mu g/m^3$ (51.9 ppb), measured 4 – 8 hours following the application. Rotondaro (2004) monitored off-site concentrations 1.5 m from the outside of three greenhouses during and following drip applications. At two of the three greenhouse sites, most concentrations were below the LOQ. At the third site, the maximum concentration was 557 $\mu g/m^3$ (82.8 ppb), measured 4 – 8 hours following the application.

Off-site concentrations are assumed to be proportional to application rate. For the studies summarized in Table 6, higher application rates are allowed on current product labels for each application method. Table 7 summarizes the maximum concentration in each study, adjusted for maximum rate allowed in California. Four of the data sets summarized in Table 6 were omitted from Table 7: 1) the bedded tarped application monitored by ARB (2003c), with samplers positioned 265 m from the treated field; 2) the bedded tarped application monitored

by ARB (2004), in which the highest concentration occurred in background samples; 3 and 4) two of the three greenhouse drip applications monitored by Rotondaro (2004), in which most samples were below the LOQ.

Table 7. Off-Site Chloropicrin Concentrations Associated with Soil Fumigation, Adjusted for Maximum Application Rate

Application Method	Sampler Distance (meters) [a]	Field Size (acres) [b]	Study Application Rate (lbs/acre) [c]	Maximum Application Rate (lbs/acre) [c]	Sample Interval (hours)	Reported Maximum Concentration ($\mu g/m^3$) [d]	Adjusted Maximum Concentration ($\mu g/m^3$) [e]
Broadcast non-tarped [f]	18	8.01	171	500	6.5	1,820	5,322
Broadcast tarped [f]	35	7.97	332	500	6.0	968	1,458
Broadcast tarped [g]	18	8.35	343	500	6.0	677	987
Broadcast tarped [h]	18	8.18	346	500	13.0	868	1,254
Bedded non-tarped [f]	18	8.46 [i]	86	250	6.0	1,760	5,116
Bedded tarped [f]	18	5.92 [j]	189	500	6.1	1,810	4,788
Bedded tarped drip [k]	20	8.2 [l]	188	300	8.4	415	622
Bedded tarped drip [m]	15	8.67 [n]	156	300	4.0	349	671
Greenhouse drip [o]	1.5	0.831 [p]	166	300	6.0	577	1,043

[a] Sampler distance from edge of treated plot; greenhouse drip distance from edge of greenhouse.
[b] For bedded applications, the total acres are reported, including furrows as well as beds; where available, treated acres are listed in footnotes below. Multiply value by 0.405 to get area in hectares (ha).
[c] For bedded applications, the reported rate is for the total acres, including furrows as well as beds. Beds reduce treated acres by 50 – 58%. The maximum application rate is the highest allowed for that method on any current product label in California. Multiply value by 1.123 to get rate in kilograms per hectare (kg/ha).
[d] Highest measured concentration associated with the application. Multiply value by 0.1487 to get result in parts per billion (ppb).
[e] Calculated by multiplying highest reported rate by ratio of maximum application rate to study application rate (assumes that concentration is proportional to application rate).
[f] Fumigant consisting of 99.4% chloropicrin was applied to plots near Phoenix, Arizona (Beard *et al*., 1996).
[g] Fumigant consisting of 99.4% chloropicrin was applied to a field in Washington (Beard *et al*., 1996).
[h] Fumigant consisting of 99.1% chloropicrin was applied to a field in Florida (Beard *et al*., 1996).
[i] 4.86 acres treated.
[j] 2.96 acres treated.
[k] Fumigant consisting of 94% chloropicrin was applied to a California field (ARB, 2006).
[l] No information given about bed width or acres treated.
[m] Fumigant consisting of 99.1% chloropicrin was applied to a California field (Rotondaro, 2004).
[n] 4.5 acres treated.
[o] Fumigant consisting of 99.1% chloropicrin was applied to beds in a California greenhouse (Rotondaro, 2004).
[p] 0.0741 acres treated.

The distance of the sampler where the highest concentration occurred is included in Table 7, as is the field size; higher concentrations would be anticipated if samplers had been positioned closer to the treated fields or if larger fields had been treated (Barry, 2005b). Sampling intervals associated with the maximum concentration are also listed in Table 7, and

ranged from 4.0 to 13.0 hours. Shorter sampling intervals under the same conditions (size, application method, rate) would result in higher concentrations (Barry, 2000).

Field Volatility (Flux)

In the field volatility studies available to DPR, flux of chloropicrin was estimated by a direct measurement method using a central gradient sampling mast supporting multiple samplers (Beard *et al.*, 1996; Rotondaro, 2004). Air samples were collected with XAD-4 solid sorbent tubes having 400 mg sorbent in the front section and 200 mg in the back section; tubes were connected to pumps calibrated at 50 ml/min. Chloropicrin was analyzed by gas chromatography with a nickel-63 electron capture detector.

Beard *et al.* (1996) characterized flux during four types of applications to fields in Arizona: broadcast tarped, bedded tarped, broadcast non-tarped, and bedded non-tarped. Flux was also profiled during broadcast tarped applications to fields in Washington and Florida; the flux was lower following these applications, and they are not considered further in this exposure assessment other than in comparison with results from the Arizona application. In the center of each treated plot, a gradient sampling mast supported six air samplers at 15, 33, 55, 90, and 150 cm above the treated soil surface; two samplers were collocated at 150 cm. Two masts were located near each other, and alternated in sequential sampling intervals; this allowed continuous monitoring when samplers were changed. Monitoring lasted 6 hours per sample during the first 48 hours, and 12 hours per sample for an additional 12 days (14 days total). The non-tarped bedded application was monitored for 7 rather than 14 days.

Quality assurance consisted of laboratory and field spikes (sampling tubes fortified with known amounts of chloropicrin), solvent blanks, and controls. Field spikes were fortified at the start of each monitoring period by injecting 1-5 µl of chloropicrin dissolved in hexane; after the solvent was evaporated, tubes were attached to sampling pumps and air was drawn through them throughout the monitoring periods. During analysis, each batch of samples was co-analyzed with a solvent blank, control tube, and laboratory spikes that were fortified before analysis (but not connected to a sampling pump). Laboratory spikes are included as a check on the analytical procedure, and field spikes are checks on environmental conditions and potential interferences during sample collection, transport, storage, and analysis. The mean percent recovery $\pm$ standard deviation (SD) of recoveries from laboratory spikes were 87 $\pm$ 17%, 93 $\pm$ 24%, and 85 $\pm$ 21% for analyses of samples collected in Arizona, Washington, and Florida, respectively.

For the purpose of adjusting results for field spike recoveries, data from the three sites were considered separately because monitoring was conducted at different times; additionally, at the Arizona site data from non-tarped and tarped applications were considered separately, as monitoring of the two types of applications occurred at different times. Field spike recoveries were generally acceptable at the Arizona and Florida sites, where mean recoveries ranged 78 – 107%. At the Washington site, mean field spike recoveries were acceptable for the mid- and high-level spikes, at 118% and 109%, respectively. Mean $\pm$ SD of low-level field spikes at the Washington site was 164 $\pm$ 65, and the range was 79.5 – 384%. Ranges of mid- and

high-level spikes at the Washington site were 44.2 – 193% and 39.4 – 223%, respectively. Beard *et al.* (1996) adjusted sample residues for field spike recoveries that were < 100%, with residue range intervals defined by mid-points between spike levels. This approach is similar to DPR policy for adjusting data used in estimating exposure, which is in general agreement with U.S. EPA policy, in which samples are corrected for field fortification recoveries below 90% (U.S. EPA, 1992; U.S. EPA, 1998). At the Arizona sites, the flux ranged from 114 to 222 $\mu g/m^2$/sec during the highest 6-hour period, corresponding to 12 to 25 percent of the chloropicrin applied.

These three broadcast non-tarped applications represent the only flux data that are replicated. The replication allows calculation of a coefficient of variation (CV) for flux for this application method. The CV is calculated using this equation: CV = 100% x SD/mean (also called the Relative Standard Deviation). The calculations are detailed in Appendix 1. The CVs for 6-hour daytime flux, 6-hour nighttime flux, and 24-hour flux were 48.2%, 116%, and 81%, respectively.

Rotondaro (2004) characterized flux during two types of applications, field (outdoor) surface drip and greenhouse (indoor) surface drip. Barry (2005a) evaluated this study and found that, for multiple reasons, the chloropicrin measurements associated with the greenhouse drip applications were not suitable for use in estimating flux. For example, samplers were essentially located at the same distance from the application (1.5 m from the edge of the greenhouse), a distance that was also too close for effective back-calculation. Additionally, the majority of the results at one of the sites were non-detects; at that site, six of eight samplers were not near the treated area. Monitoring during the field drip application was conducted with a pair of masts, each of which supported six air samplers at 15, 33, 55, 90, and 150 cm above the treated soil surface; two samplers were collocated at 150 cm. Rotondaro (2004) reported that the total chloropicrin mass lost through field volatility was estimated at 15.2% of the applied mass. The highest flux, 70.1 $\mu g/m^2$/sec, occurred during the first 4-hour interval following the application.

Barry (2008a) calculated from the submitted studies the maximum estimated 6-hour TWA and 24-hour TWA chloropicrin soil flux densities (during both day and night sampling intervals); the highest flux values for each interval duration (6 hour and 24 hour), application method and application rate are summarized in Table 8. The 6-hour day and night intervals are considered separately because flux differs under day and night conditions. The 24-hour interval, of course, includes both day and night.

For short-term bystander exposures, Barry (2008a) calculated rate-adjusted chloropicrin air concentrations at a point 1.2 m above ground (assumed breathing zone) and 10 feet (3.0 m) from the edge of the treated area. These estimates were derived using the ISCST3 model together with "screening mode" inputs. The treated field is modeled as a square 40-acre (16-ha) area source. Barry (2008a) used the following screening level meteorological conditions for each interval: 1 m/s wind speed and Pasquill-Gifford Class D stability (maximum daytime atmospheric stability) to estimate daytime 6-hour flux; 1.0 m/s and Class F stability (moderately stable atmospheric stability) to estimate nighttime 6-hour flux; and 1.4 m/s and

Class C stability (slightly unstable daytime atmospheric stability) for 24-hour flux. The model yielded downwind centerline estimates of reasonable worst-case concentrations at any pre-determined distance from the edge of the field.

Table 8. Chloropicrin Flux Estimates Used to Estimate Off-Site Air Concentrations for Short-Term Exposures [a]

Application Method	Study Location	Study Application Rate (lbs/Acre) [b]	Study Effective Broadcast Application Rate (lbs/Acre) [c]	24-Hour Flux ($\mu g/m^2/sec$)	6-Hour Flux, Day [d] ($\mu g/m^2/sec$)	6-Hour Flux, Night [d] ($\mu g/m^2/sec$)
Broadcast non-tarped	Arizona	171	171	86	50	180
Bedded non-tarped	Arizona	149	86	66	114	113
Bedded tarped	Arizona	377	189	111	211	30
Broadcast tarped [e]	Arizona	332	332	108	132	142
Bedded drip tarped	California	300	156	22	47 [f]	5 [f]

[a] From Barry (2008a). Data from Beard *et al.* (1996), except for bedded drip tarp by Rotondaro (2004).
[b] This application rate is the "treated acre" rate. For broadcast application methods the Study Application Rate and the Study Effective Broadcast Application Rate will be the same. For bedded applications an adjustment must be made to the Study Application Rate to account for the portions of the field that are untreated, because the treated area is the top of the bed only; the furrow area between the beds is untreated. Multiply value by 1.123 to get rate in kilograms per hectare (kg/ha).
[c] The effective broadcast application rate is found by dividing the total amount of chloropicrin applied to the field by the whole area of the field, including untreated areas interspersed with the treated areas. In the case of bedded applications, the treated area is the top of the bed only, and the furrow area between the beds is untreated.
[d] The 6-hour flux is used to estimate both 6-hour and 1-hour TWA air concentrations. Then a peak-to-mean adjustment is made to the 6-hour TWA air concentrations to derive the 1-hour air concentrations (Barry, 2000).
[e] Data were available from multiple sites. Washington and Florida sites had lower flux and concentrations and are not included.
[f] These two flux estimates are 8-hour TWA due to the sampling intervals in the study.

Table 9 reports concentrations adjusted for the maximum application rates allowed on product labels currently registered in California. A single product, Metapicrin (EPA Reg. No. 8622-43-AA), allows higher application rates of up to 1,076 lbs AI/acre (1,209 kg/ha) if followed by cultipacking or water seal. No other chloropicrin product allows applications at this rate. Concentrations associated with applications of Metapicrin at this maximum rate are summarized in Appendix 2.

Lower maximum rates have been proposed for shank fumigations; some current product labels incorporate the lower rates. For the convenience of risk managers addressing products that limit use to the lower rates, Appendix 3 summarizes chloropicrin air concentrations, based on the same data and model as the concentrations in Table 9, but assuming lower application rates (Barry, 2008a). Also for the convenience of risk managers, Appendix 3 summarizes chloropicrin air concentrations at selected distances from the edge of the field,

and for 15-acre as well as 40-acre applications (where the number of acres refers to the treated area).

Table 9. Chloropicrin Off-Site Air Concentrations Used to Estimate Short-Term Exposures [a]

Application Method	Study Location	Maximum Application Rate (lbs/Acre) [b]	1-Hour, Day ($\mu g/m^3$) [c]	1-Hour, Night ($\mu g/m^3$) [c]	6-Hour, Day ($\mu g/m^3$)	6-Hour, Night ($\mu g/m^3$)	24-Hour ($\mu g/m^3$)
Broadcast non-tarped	Arizona	500 [d]	18,000	**110,000**	7,500	**44,000**	6,500
Bedded non-tarped	Arizona	250 [d]	42,000	67,000	17,000	27,000	5,000
Bedded tarped	Arizona	500	44,000	77,000	18,000	31,000	**7,400**
Broadcast tarped	Arizona	500	40,000	9,300	16,000	3,800	4,300
Bedded drip tarped	California	300	11,000	2,100	4,700	840	1,100

[a] From Barry (2008a), based on data from Beard *et al*. (1996), except for bedded drip tarp by Rotondaro (2004). Concentrations were generated with the Industrial Source Complex Short Term Version 3 (ISCST3) air dispersion model, assuming a receptor 1.2 m above ground and 10 ft (3.0 m) from the edge of a square, 40-acre treated area, and have been rounded to two significant figures. Bolded values represent the highest concentration for the exposure duration. Multiply value by 0.1487 to get result in parts per billion (ppb).

[b] Unless other wise noted, this application rate is the maximum allowed for that method on any product label currently registered in California for that use. Multiply value by 1.123 to get rate in kilograms per hectare (kg/ha).

[c] 1-hour concentrations were estimated from the 6-hour concentrations by employing a peak-to-mean ratio as described in text (Barry, 2000).

[d] One product, Metapicrin (EPA Reg. No. 8622-43-AA), allows applications of up to 1,076 lbs AI/acre if followed by cultipacking or water seal. Concentration estimates associated with this product are reported in Appendix 2.

Measurements of air concentrations are known to be sampling duration-dependent (Csanady, 1973; Pasquill, 1974). This is because real-time concentrations of an airborne chemical are heterogeneous and fluctuating. When a sample is collected, the final value is an average of all the variations in air concentration over the continuous period of sample collection. With shorter sampling durations, any extreme values will have a greater impact on the value of the final concentration than with longer sampling durations. Health-protective estimates will thus be higher for shorter durations. The shortest monitoring interval for flux in any chloropicrin study was 6 hours, and 1-hour concentrations were estimated from the 6-hour concentrations by employing a peak-to-mean ratio using the following equation (Barry, 2000):

$$C_p = C_m(t_p/t_m)^{-1/2}$$

Where:

C_p = peak concentration over period, t_p, of interest
C_m = mean concentration over measurement period, t_m
t_p = duration of peak period of interest
t_m = duration of mean measurement period

Due to equipment limitations, during pre-plant soil fumigations approximately 40 acres (16 ha) can be treated in a single workday. Larger fields may be treated on consecutive days (a practice commonly referred to as "rolling applications"). When this occurs, a bystander can potentially be located downwind of an application occurring that day, as well as another area treated the previous day. Barry (2008b) provided estimates of concentrations a bystander might be anticipated to encounter when downwind of a field currently being treated, with another field upwind having been treated the previous day. These estimates are summarized in Appendix 4.

The 24-hour TWA concentrations in Table 9 assume that an individual is located downwind throughout the exposure interval. For repetitive exposures over longer intervals of weeks or months, that assumption is not realistic, however. For seasonal and annual bystander exposure estimates, concentrations are needed that reflect the reality of changing wind directions. Barry (2008c) estimated 2-week TWA concentrations to be used in estimating seasonal and annual bystander exposures, by first calculating an average 24-hour flux over 2 weeks, then adjusting with a time-scaling factor derived using peak-to-mean theory based on both empirical and theoretical studies. These concentrations are summarized in Table 10.

Table 10. Chloropicrin Off-Site Air Concentrations Used to Estimate Seasonal and Annual Exposures [a]

Application Method	Study Location	Study Effective Broadcast Application Rate (lbs/Acre) [b]	Assumed Typical Application Rate (lbs/Acre) [c]	2-Week Flux ($\mu g/m^2/sec$) [d]	Percentage of Applied Mass Lost Over 2-Week Interval [e]	2-Week Average Concentration ($\mu g/m^3$)
Broadcast non-tarped	Arizona	171	175	10.39	62	130
Bedded non-tarped	Arizona	86	175	5.39	61	140
Bedded tarped	Arizona	189	350	21.45	69	**490**
Broadcast tarped	Arizona	332	350	12.37	63	160
Bedded drip tarped	California	156	300	2.24	15	54

[a] From Barry (2008c), based on data from Beard *et al.* (1996), except for bedded drip tarp by Rotondaro (2004). Concentrations were generated with the Industrial Source Complex Short Term Version 3 (ISCST3) air dispersion model, assuming a receptor 1.2 m above ground and 10 ft (3.0 m) from the edge of a square, 40-acre treated area, and have been rounded to two significant figures. Bolded value represents the highest concentration for this exposure duration.

[b] This is the application rate used in the study; for bedded applications the effective broadcast application rate is found by dividing the total amount of chloropicrin applied to the field by the area of the entire field, rather than just the area treated, because the treated area is the top of the bed only, and the furrow area between the beds is untreated. Multiply value by 1.123 to get rate in kilograms per hectare (kg/ha).

[c] This application rate is assumed to be a typical rate. It is the maximum rate supported by registrants, and is the rate assumed in the U.S. EPA human health risk assessment (Reaves and Smith, 2008).

[d] This is the average 24-hour flux over the 2-week flux profile, adjusted for variation in weather conditions.

[e] This is the mass projected to be emitted over a 2-week interval, reported as percent of applied mass (Beard *et al.*, 1996; Rotondaro, 2004).

Rather than adjust application rates to the maximum allowed on current product labels, for long-term exposures application rates that are considered typical, as assumed by U.S. EPA, were used instead (Reaves and Smith, 2008). Table A3-7 in Appendix 3 summarizes cumulative percentile application rates, calculated from pounds chloropicrin applied and acres treated in chloropicrin applications as reported in the PUR (DPR, 2009). Over the 5-year interval 2003-2007, the annual 50th percentile ranged between 111 and 188 lbs AI/acre, while the 95th percentile was 200 – 235 lbs AI/acre. Applications reported in the PUR do not include application method. Given that these percentiles include tarped and non-tarped, broadcast and bedded methods, they suggest that average application rates for each method do not exceed the rates assumed to be typical as listed in Table 10.

Barry (2008c) also provided estimates of the proportion of applied mass that was lost in 2 weeks; these are listed as percentages in Table 10.

Application Site Air – Structural Fumigation

ARB monitored off-site concentrations of chloropicrin during three structural fumigations with sulfuryl fluoride, in which chloropicrin was used as a warning agent (ARB, 2003d; 2005a; 2005b). These studies are summarized in Table 11. These data form the basis for estimating exposures of bystanders to structural fumigation. In two of these studies (ARB, 2003d; 2005a), indoor air samples were collected for 24 hours following aeration; exposures of individuals in fumigated structures are based on these data.

Table 11. Chloropicrin Off-Site Air Concentrations Measured During Structural Fumigations in California [a]

Study Location (County)	Dates	Sampler Distances (m) [b]	Total Samples [c]	LOQ (µg/sample) [d]	Samples ≥ LOQ	Maximum Concentration (µg/m^3) [e]
Sacramento [f]	10/28/02 – 11/3/02	1.5 – 18	140	0.0198	65	29
Nevada [g]	7/18/04 – 7/24/04	1.5 – 12	178	0.0198	97	43
Placer [h]	6/24/04 – 7/4/04	1.5 – 12	132	0.0198	42	21

[a] All fumigations involved tarped houses; monitoring conducted by the Air Resources Board.
[b] Sampler distance from edge of tarped house. In each study, samplers were placed in three concentric rings with four samplers in each ring.
[c] Includes four background samples collected before fumigation; all background results were < LOQ.
[d] LOQ: Limit of Quantification. In the study reports, this is called the "estimated quantitation limit," or EQL.
[e] Highest measured chloropicrin concentration associated with the application; results have not been corrected for spike recoveries. Multiply value by 0.1487 to get result in parts per billion (ppb).
[f] From ARB (2003d). Chloropicrin used as a warning agent during sulfuryl fluoride fumigation of a 22,000-ft^3 house; total amount chloropicrin 1.5 ounces for a nominal indoor concentration of 68 µg/m^3. Fumigation duration was 48 hours, followed by a 45-minute mechanical venting interval and 22-hour aeration.
[g] From ARB (2005a). Chloropicrin used as a warning agent during sulfuryl fluoride fumigation of an 81,000-ft^3 house; total amount chloropicrin 6 ounces for a nominal indoor concentration of 74 µg/m^3. Fumigation duration was 71 hours, followed by an 83-minute mechanical venting interval and 72-hour aeration.
[h] From ARB (2005b). Chloropicrin used as a warning agent during sulfuryl fluoride fumigation of a 45,000-ft^3 house; total amount chloropicrin 3 ounces for a nominal indoor concentration of 65 µg/m^3. Fumigation duration was 43.5 hours, followed by a 50-minute mechanical venting interval and 72-hour aeration.

In all three studies, samplers consisted of 8 mm x 140 mm adsorbent tubes containing 400 mg XAD-4 resin, with a back-up section of 200 mg of XAD-4 resin to verify that no breakthrough occurred, connected to sampling pumps with Teflon tubing and fittings. The pump flow rate was 90 standard cubic centimeters per minute in the first study (ARB, 2003d), and 100 standard cubic centimeters per minute in the second and third studies (ARB, 2005a; 2005b). Pump rates were calibrated with a digital mass flowmeter at the start and end of each sampling interval. Sampler intakes were approximately 1.5 m above ground.

The first study was conducted in 2002 in Sacramento County, and monitored off-site chloropicrin concentrations during fumigation of a single-story, 1,375-square-foot house (ARB, 2003d). The estimated volume for fumigation was 22,000 ft^3 (620 m^3). Quality assurance consisted of replicate sampling, a single trip blank, and four trip, field, and laboratory spikes. Collocated duplicate samples were collected at a sampler 1.5 m east of the house during each sampling interval. In the seven sample pairs with results > LOQ, the collocated samples differed 5 – 63%, with an average difference of 20%. No chloropicrin was detected in the background samples or the trip blank. The mean recovery of four 0.225-μg field spikes was 83%. The highest reported concentration was 29 $\mu g/m^3$, occurring during the mechanical ventilation interval; the sampling interval was 1.5 hours. Corrected for the mean field spike recovery of 83%, this result would be 35 $\mu g/m^3$.

The second study was conducted in 2004 in Nevada County, and monitored off-site chloropicrin concentrations during fumigation of a two-story house (ARB, 2005a). The estimated volume for fumigation was 81,000 ft^3 (2,300 m^3). Quality assurance consisted of replicate sampling, a single trip blank, and four trip, field, and laboratory spikes. Collocated duplicate samples were collected at a sampler 1.5 m north of the house during each sampling interval. In the nine sample pairs with results > LOQ, the collocated samples differed 0 – 36%, with an average difference of 11%. No chloropicrin was detected in the background samples or the trip blank. The mean recovery of four 0.228-μg field spikes was 79%. The highest reported concentration was 43 $\mu g/m^3$, occurring during the mechanical ventilation interval at a sampler located 1.5 m northwest of the house; the sampling interval was 1.5 hours. Corrected for the mean field spike recovery of 79%, this result would be 54 $\mu g/m^3$. Data from this study were used to estimate exposures of bystanders to a structural application, and concentrations measured at samplers in this study are summarized in Table 12.

The third study was conducted in 2004 in Placer County, and monitored off-site chloropicrin concentrations during fumigation of a two-story house (ARB, 2005b). The estimated volume for fumigation was 45,000 ft^3 (1,300 m^3). Quality assurance consisted of replicate sampling, a single trip blank, and four trip, field, and laboratory spikes. Collocated duplicate samples were collected at a sampler 1.5 m north of the house during each sampling interval. In the seven sample pairs with results > LOQ, the collocated samples differed 2 – 15%, with an average difference of 9.9%. No chloropicrin was detected in the background samples or the trip blank. The mean recovery of four 0.228-μg field spikes was 77%. The highest reported concentration was 21 $\mu g/m^3$, occurring during the mechanical ventilation interval; the

sampling interval was 1.25 hours. Corrected for the mean field spike recovery of 77%, this result would be 27 μg/m^3.

Table 12. Off-Site Chloropicrin Concentrations Associated with a Structural Fumigation [a]

Sampling Interval	Sample Duration (Hours)	East Sampler (μg/m^3)	North Sampler (μg/m^3)	NE Inner Sampler (μg/m^3)	NE Outer Sampler (μg/m^3)	NW Inner Sampler (μg/m^3)	NW Inner Colloc [b] (μg/m^3)	West Sampler (μg/m^3)
Distance (m) [c]		3.0	3.0	1.5	12	1.5	1.5	3.0
1 - exposure day	6.25	1.70	3.45	2.68	0.792	9.61	8.26	*0.284*
2 - exposure night	11.5	0.629	1.38	0.466	*0.138*	3.85	3.58	1.32
3 - exposure day	12.5	0.769	1.37	1.40	0.332	3.68	2.89	0.448
4 - exposure night	11.5	0.553	*0.143*	*0.143*	*0.142*	0.902	1.02	*0.142*
5 - exposure day	12.5	0.432	0.629	0.724	*0.133*	1.63	1.66	0.414
6 - exposure night	11.5	0.332	*0.140*	*0.141*	*0.141*	0.962	0.932	*0.141*
7 - exposure day	6.0	*0.274*	*0.282*	0.655	*0.272*	0.988	0.952	*0.282*
8 - mechanical vent	1.5	11.7	14.8	13.7	3.31	43.3	30.1	*0.975*
9 - aeration day	5.0	0.776	1.11	1.01	*0.342*	1.63	1.90	*0.342*
10 - aeration night	11.5	*0.142*	*0.141*	*0.140*	*0.145*	*0.144*	*0.138*	*0.145*
11 - post-day	12.5	*0.129*	*0.130*	*0.130*	*0.130*	0.302	0.305	*0.129*
12 - post-night	11.25	*0.146*	*0.149*	*0.149*	*0.149*	*0.144*	*0.146*	*0.145*
13 - post day	12.75	*0.128*	*0.129*	*0.129*	*0.126*	0.275	0.128	*0.127*

[a] From ARB (2005a). Concentrations have not been corrected for recoveries. For results below the limit of quantification (LOQ), ½ LOQ was reported; these values are italicized. The LOQ was 0.0198 μg/sample. Results are omitted for the Northwest Outer Sampler, which had only one result above the LOQ (2.34 μg/m^3 during Interval 2), and for five other samplers (South, SE Inner, SE Outer, SW Inner, and SW Outer) where all results were below the LOQ. Multiply concentrations by 0.1487 to get results in parts per billion (ppb).

[b] This sampler was collocated with the NW Inner Sampler.

[c] Sampler distance from edge of the house being fumigated, in meters.

Table 13 summarizes the short-term concentrations used to estimate bystander exposures associated with structural fumigation. All concentrations reported in Table 13 are from a sampler located 1.5 m northwest of the structure being fumigated in the second study (ARB, 2005a). However, the amount of chloropicrin used in the fumigation was 6 ounces (180 ml); the maximum rate stated on the label is 1 ounce (30 ml) per 10,000 ft^3 (280 m^3), which would be 8 ounces (240 ml) in the 81,000-ft^3 (2,300-m^3) structure. The concentrations reported in the last column of Table 13 were adjusted to account for the submaximal rate by multiplying by 8/6 = 1.33.

Table 13. Concentrations Used to Estimate Exposure of Bystanders to Chloropicrin from Structural Fumigation [a]

Duration	Sample Interval (Hours)	Chloropicrin in Sample (µg/sample)	Volume Sampled (m^3)	Measured Concentration ($\mu g/m^3$) [b]	Corrected Concentration ($\mu g/m^3$) [c]
1 Hour	1.6	0.416	0.0096	43	73
8 Hours [d]	6.5	0.474	0.039	12	16
24 Hours [e]	24.0	0.545	0.146	3.7	6.2

[a] Off-site concentrations measured during sulfuryl fluoride structural fumigation with chloropicrin as a warning agent. Highest off-site concentrations for each duration were from a sampler located 1.5 m northwest of the structure being fumigated (ARB, 2005a).
[b] Time-weighted average concentration from ARB (2005a).
[c] Concentration corrected for 79% field spike recovery and multiplied by 8/6 because chloropicrin use in monitoring study was below the maximum rate specified for warning agent use on the sulfuryl fluoride product label.
[d] Highest rolling 8-hour concentration, calculated from consecutive 1.6- and 4.9-hour concentrations: Measured concentration = [0.416 µg/sample + 0.0598 µg/sample]/[0.0096 m^3 + 0.0294 m^3].
[e] Highest rolling 24-hour concentration, calculated from consecutive 12-hour concentrations.

Water

Chloropicrin is on the list of pesticides that are considered to have the potential to contaminate ground water (Clayton, 2005). Chloropicrin is on this list based on its fairly high water solubility, its low soil adsorption coefficient (K_{oc} = 25 cm^3/g), and the relatively long half-life reported for hydrolysis, which data suggest exceeds 191 days (Clayton, 2005).

Although chloropicrin has certain physicochemical properties that might predispose it to leach into ground water, in extensive monitoring there have been no verified detections of chloropicrin in California's ground water. DPR has not conducted any well monitoring for chloropicrin in California; however, DPR has included in its groundwater monitoring database results from sampling conducted by other agencies. The database, including criteria for selection of wells and sampling and analytical methods, is described by Troiano *et al.* (2001). Between 1986 and 2003, a total of 1,719 well water samples collected in 34 California counties (out of 58 counties total) were tested for the presence of chloropicrin (Schuette *et al.*, 2003), and chloropicrin was not detected in any of these samples. Well water sampling for chloropicrin has not been reported since 2003.

ENVIRONMENTAL FATE

DPR released an Environmental Fate Review for chloropicrin in 1990 (Kollman, 1990). This section briefly summarizes and updates information from that review. Following application to soil, chloropicrin rapidly diffuses through the soil in all directions, then dissipates quickly, with half-lives ranging from approximately an hour to several days. Volatilization is the major pathway through which chloropicrin dissipates from soil, but chloropicrin is also degraded through biotic and abiotic reactions. In water, chloropicrin can persist for several days in the absence of light, but it degrades rapidly when subjected to light of suitable

wavelengths, with half-lives ranging from 6 hours to 3 days. Under reducing conditions, chloropicrin also reacts quickly, undergoing reductive dechlorinations. In air, chloropicrin is reactive, undergoing photodegradation to phosgene and nitrosyl chloride with an estimated half-life of 18 hours.

Persistence in Soil Environment

As a soil fumigant, chloropicrin is applied to soil via either injection with shank or similar equipment, or via drip irrigation. After application to soil, chloropicrin rapidly diffuses through the soil in all directions, although it moves less rapidly than the more volatile methyl bromide (Wilhelm, 1960; Youngson *et al.*, 1962; Gan *et al.*, 2000; Desager *et al.*, 2004). Volatilization from soil is the major off-site loss pathway, followed by chemical degradation and microbial decomposition (Gou *et al.*, 2003). Chloropicrin disappearance from treated soils is well-described by first-order kinetics (Gan *et al.*, 2000; Ibekwe *et al.*, 2004; Zhang *et al.*, 2005).

Volatilization from Soil

Both the vapor pressure and Henry's Law Constant for chloropicrin are relatively high, 23.2 mm Hg and 2.5 x 10^{-3} atm-m^3/mole, respectively, at 25°C (See Table 1). Field volatility data suggest that substantial proportions of applied chloropicrin are emitted from soil. Field volatility studies reported by Beard *et al.* (1996) and Rotondaro (2005) were summarized above in the Environmental Concentrations section. As listed in Table 10, in these studies it was determined that over 2-week intervals, on average 61 – 69% of the chloropicrin applied by shank fumigation volatilized, while 15% of chloropicrin applied by tarped drip fumigation volatilized over 2 weeks.

Abiotic and Microbial Reactions with Chloropicrin in Soil

Chloropicrin is rapidly degraded in soil under both aerobic and anaerobic conditions (Olson and Lawrence, 1990a and 1990b; Wilhelm *et al.*, 1996; Gan *et al.*, 2000). Field dissipation studies reported degradation half-lives between 1 and 8 days, depending on the formulation, application method and soil type (Ivancovich *et al.*, 1990). Studies of soil repeatedly treated with chloropicrin suggest that enrichment can occur of the microorganisms capable of degrading chloropicrin (Ibekwe *et al.*, 2004; Zhang *et al.*, 2005).

Laboratory soil metabolism studies also report chloropicrin degradation half-lives in the range of a few hours to several days. The estimated half-life when 250 ppm of ^{14}C-radiolabeled chloropicrin was incubated with sandy loam under aerobic conditions was approximately 5 days; about 70% of the applied radiolabel was recovered by the 90th day of the study as CO_2, while most of the rest was volatilized chloropicrin (Olson and Lawrence, 1990a). In an anaerobic soil metabolism study, Olson and Lawrence (1990b) incubated 250 ppm chloropicrin with sandy loam under aerobic conditions for 5 days post-application (i.e., the aerobic half-life); the soil was then made anaerobic by flushing with nitrogen gas 5 days post-application. Although a half-life was not calculated for chloropicrin under anaerobic conditions because the only sampling intervals were 30 and 60 days after the soil was made anaerobic, Olson and Lawrence (1990b) reported that dissipation was "rapid." The anaerobic

half-life was assumed to be shorter than 10 days, as no parent chloropicrin was recovered 35 days post-application (Lawrence, 1990). As with the aerobic soil metabolism study, the radiolabel was predominantly recovered in CO_2 and the parent compound, with CO_2 averaging up to 16.4% of the total applied. However, total recovery of the radiolabel was poor, ranging from an average of 50.2% immediately following treatment to an overall mean total recovery of 74.3% on the 30^{th} and 60^{th} days post-application. Olson and Lawrence (1990b) concluded that losses occurred during the sampling procedure.

In a laboratory study, chloropicrin degraded rapidly when incubated in 100-g samples of Wooster sandy loam collected from Ohio (Craine, 1985b). Aliquots of a chloropicrin solution consisting of 11.35 mg in 1 ml ethanol were pipetted into flasks containing 100 g of soil. Flasks were incubated in the dark at 25°C under aerobic conditions and sampled hourly for 24 hours; concentrations of chloropicrin and inorganic chloride were determined in the samples. Within the first hour, the chloropicrin was reduced to 48.7% of the initial dose, yielding an estimated half-life of about 1 hour. After 24 hours, approximately 91% of the chloropicrin had degraded. Conversion of chloropicrin to inorganic chloride had an estimated half-life of 9.9 hours. Craine (1985b) also investigated anaerobic metabolism of chloropicrin; water was added to the flasks to induce anaerobic conditions. The mean chloropicrin degradation half-life was reported to be 17 hours in the soil-water slurries.

Wilhelm *et al.* (1996) reported on an aerobic soil metabolism study in which 50-g sandy loam soil samples were treated with ^{14}C-chloropicrin at a rate equivalent to 500 lbs AI/acre (562 kg AI/ha), then incubated in the dark at 25°C. Samples were collected after 4.5 hours, and at 1, 2, 3, 6, 14, 21, and 24 days post-dose. Overall recovery was 97.2% of the applied radiolabel. The estimated half-life for chloropicrin was 4.5 days. After 24 days, up to 75.2% of the applied radiolabel was recovered as ^{14}C-CO_2.

Gan *et al*. (2000) investigated the aerobic metabolism of chloropicrin in 10-g samples of three soils, including Arlington sandy loam from California, Carsitas loamy sand from California, and Waukegen silt loam from Minnesota, with respective organic matter content of 0.92%, 0.22%, and 3.1%. In all three soils (with initial water content adjusted to 10%), chloropicrin degradation increased 7- to 11-fold as soil temperatures increased in the range 20°C – 50°C. In contrast, variation of soil moisture content, which was tested only in Arlington and Carsitas soils, had little effect. With soil temperatures held at 20°C, and soil moisture ranging 1.8% – 16%, degradation in chloropicrin doubled from the high to low moisture contents in Arlington sandy loam, but did not change across the same moisture range in Carsitas loamy sand. In a laboratory study with loamy sand from a Wisconsin nursery, Zhang *et al.* (2005) found no change in chloropicrin degradation rates when moisture ranged 0.5% – 10%, but the degradation was significantly lower at a moisture content of 15%.

Gan *et al*. (2000) found that degradation was slower in sterile soil: in untreated, air-dried soil, the half-life was 1.5, 4.3, and 0.2 days for the Arlington, Carsitas and Waukegen soils respectively, while in autoclaved soils the respective half-lives were 6.3, 13.9, and 2.7 days. Based on the difference in the degradation between the sterile and non-sterile soils, Gan *et al*. (2000) estimated that microbial degradation accounted for 68 – 92% of the chloropicrin

degradation. In similar studies, Zheng *et al.* (2003) estimated that microbial degradation of chloropicrin in a sandy loam from California accounted for 84% of the total chloropicrin degradation, and Zhang *et al.* (2005) estimated the microbial contribution to chloropicrin degradation in loamy sands from Wisconsin and Georgia to range between 40% and 80%.

Chloropicrin is degraded in soil by *Pseudomonas* bacteria via a metabolic pathway involving dehalogenated intermediates dichloronitromethane, chloronitromethane, and nitromethane, apparently formed in sequence (Castro *et al.*, 1983):

$$CCl_3NO_2 \Rightarrow CHCl_2NO_2 \Rightarrow CH_2ClNO_2 \Rightarrow CH_3NO_2$$

Alternately, Cervini-Silva (2000) found evidence that formation of dichloronitromethane and chloronitromethane can occur simultaneously via abiotic oxidation-reduction reactions in the presence of strong electron donors such as those found in iron-bearing soils.

Other reaction products of chloropicrin in soil have been documented as well. Spokas and Wang (2003) noted increased emissions of nitrous oxide (N_2O) following soil fumigation with chloropicrin, in both laboratory and field studies; in the field, daily N_2O emissions increased 7-fold during the first 10 days post-fumigation before decreasing to background levels. Follow-up laboratory studies using radiolabels and microbial inhibitors caused Spokas *et al.* (2006) to conclude that in the Georgia loamy sand treated in their studies, about 20% of the increased N_2O production could be attributed to microbes sensitive to tetracycline and streptomycin, while 70% – 80% was due to fungi sensitive to cycloheximide and benomyl. Following studies in which chloropicrin was incubated with steam-sterilized soil, Spokas *et al.* (2006) concluded that at most 18% of the increase in N_2O was from abiotic reactions, although they could not verify that sterilized soil did not have residual biotic activity. ^{15}N-labeled chloropicrin yielded a significant increase of ^{15}N-N_2O, yet only about 12% of the ^{15}N-N_2O was calculated to come from chloropicrin mineralization; most of the ^{15}N came from other pools in the treated soil (Spokas *et al.*, 2006). Increasing the oxygen content in the headspace of the incubation vials to 30% further increased N_2O, to about 5-fold greater than amounts occurring when chloropicrin was incubated at ambient oxygen concentrations. Although chloropicrin increases production of N_2O, no increased production of nitrogen, CO_2 or methane occurred in soils incubated with chloropicrin in comparison to soils incubated without chloropicrin (Spokas *et al.*, 2005; Spokas *et al.*, 2006).

Adsorption to Soil

The soil/water adsorption coefficient (K_d; ratio of chemical concentrations in soil and water) of chloropicrin was investigated in a series of laboratory experiments with 50-g samples of four soil types, including commercially purchased agricultural sand, Canfield sandy loam, Wooster sandy loam, and Holly sandy loam (Craine, 1985c). Other than the purchased sand, soils were collected from several locations near Ashland, OH, and sifted through 0.25-inch (0.64-cm) mesh. The sandy loams were misidentified by Craine (1985c) as silt loams, but the correct soil texture can be determined using a nomogram in USDA (2007). The organic matter content of the soils was 0.3% for the agricultural sand, 5.5% for the Canfield sandy

loam, 7.2% for the Wooster sandy loam, and 7.4% for the Holly sandy loam. Chloropicrin in an ethanol solution was added in amounts ranging from 9 to 127 mg/kg soil. A soil-free control bottle containing the same amount of chloropicrin as the soil samples was used to determine loss of chloropicrin during the sampling procedure, which ranged 26% – 50% of the amount applied, and the amount of chloropicrin that degraded in soil samples, which ranged 10% – 61%. After the 1-hour incubation period, 200 ml water was added to flasks, and the amount of chloropicrin in water and soil was determined. The estimated chloropicrin adsorbed to soil ranged from 2.8% – 16.2%. The mean K_d ranged from 0.179 to 0.311 for the sandy loam soils and was 0.273 for the agricultural sand; the mean soil absorption coefficient (K_{oc}; soil adsorption normalized to soil organic matter content) was 25 cm^3/g (calculated by DPR's Environmental Monitoring Branch, internal database). In a subsequent communication, Craine (1986) noted that because of the "rapid rate at which chloropicrin is metabolized in soil," no equilibrium between adsorption and desorption could be established in the 1-hour interval monitored in this study.

Kenaga (1980) calculated a K_{oc} of 62 for chloropicrin, based on a reported water solubility of 2,270 ppm. The calculation used a regression of K_{oc} on water solubility for 170 chemicals. The regression equation was $K_{oc} = 3.64 – 0.55$(log water solubility).

Although chloropicrin rapidly dissipates from soil under many conditions, in some cases residual amounts can persist. For example, Guo *et al.* (2003b) report a case in which soil beneath a facility in Maine that had formerly manufactured chloropicrin contained residues as high as 500 mg/kg 7 years after manufacturing ceased and the facility was abandoned. Chloropicrin concentrations in groundwater beneath the facility ranged 10 – 150 mg/l (Guo *et al.*, 2003b).

To investigate chloropicrin's persistence in soil, Guo *et al.* (2003a) conducted a laboratory study with triplicate 10-g samples of sandy loam, loam, and silt loam soils from California and Pennsylvania. Samples were mixed with chloropicrin at an initial concentration of 1,690 mg/kg (i.e., 10 µl chloropicrin in 10 g soil) and incubated in the dark at 20°C for 30 days. Following incubation, soils were thinly spread onto foil sheets in a fume hood, and residues were allowed to evaporate for 20 hours, after which the remaining residues were extracted. The average residues extracted from the incubated soil ranged from 0.7% in the sandy loam to 4.0% in the silt loam. Extending the evaporation from 20 hours to 120 hours had little effect on the persistent residues, nor did shortening the incubation time to 10 days. Soils incubated for less than 10 days had lower persistent residue levels.

Leaching from Soil

Laboratory data suggest that under some conditions chloropicrin residues could leach into ground water. Guo *et al.* (2003b) investigated the leaching potential of persistent chloropicrin residues in silt loam from Pennsylvania. Triplicate samples of soil were mixed with chloropicrin at an initial concentration of 845 mg/kg (i.e., 150 µl chloropicrin in 330 g soil) at 20°C for 35 days. Following incubation, soils were thinly spread onto foil sheets in a fume hood, and residues were allowed to evaporate for 48 hours. Aliquots of this treated soil were

mixed with deionized water (10 g soil, 8 ml water). After an additional 24 hours, the mixtures were centrifuged (at 956 x gravity for 15 minutes), and an average of 2.10 mg/l chloropicrin was quantitated in the supernatant. Follow-up soil column studies by Guo *et al.* (2003b) suggested that under conditions of high water movement through soil and limited microbial activity, substantial amounts of chloropicrin could potentially leach into ground water.

Persistence in Water Environment

Chloropicrin persists in water for several days in the absence of light, but degrades rapidly when subjected to light of suitable wavelengths, with half-lives ranging from 6 hours to 3 days (Castro and Belser, 1981; Chang, 1989; Moreno and Lee, 1993). Under reducing conditions, chloropicrin undergoes a series of reductive dechlorinations (Zheng *et al*., 2006; Lee *et al*., 2008). In addition to leaching from pesticide applications, chloropicrin is also formed in water with high organic content as a byproduct of certain disinfection chemicals, although environmental concentrations are invariably low. The potential for chloropicrin to bioconcentrate in aquatic organisms is also anticipated to be low.

Hydrolysis

Craine (1985a) investigated chloropicrin hydrolysis in 250-ml aliquots of aqueous solutions at pH 5, 7 or 9. The solutions, with initial chloropicrin concentrations of 110 mg/l, 42.1 mg/l, and 205 mg/l, respectively, were incubated in sealed 550-ml Erlenmeyer flasks in the dark at either 25°C or 35°C for 29 days. Preliminary experiments without water showed that flasks would retain chloropicrin for 29 days, although "inconsistent" chloropicrin losses occurred during headspace sampling. Samples of headspace gases and of solution were collected at 0, 2, 4, 9, 14, 21, and 29 days. Chloroform was detected in trace amounts in several flasks, at all three pH levels. No other organic degradation products were detected by gas chromatography with either ^{63}Ni or flame ionization detectors; reference standards of chloropicrin, chloroform, methane, methanol, and nitromethane were used to calibrate the detectors. Inorganic chloride in the solutions was quantitated with an ion-specific electrode, and was corrected for amounts initially present in the buffered solutions. Recognizing that each chloropicrin molecule contains three chlorine atoms, the theoretical maximum inorganic chloride concentration in each solution could be calculated from the initial chloropicrin concentration. The highest measured amount of inorganic chloride in each solution ranged from 0.8% of the theoretical maximum at pH 5 and 25°C to 63.3% of the theoretical maximum at pH 7 and 35°C. Craine (1985a) calculated rates of hydrolysis at each pH and temperature; in general, rates increased with temperature and pH, with the slowest rate at pH 5 and 25°C (0.8 μmol/liter/day) and the highest at pH 9 and 35°C (165.2 μmol/liter/day).

In contrast to Craine (1985a), Chang (1989) found limited hydrolysis of chloropicrin in 100-mg/l aqueous solutions at pH 5, 7 and 9. To prevent volatilization, all vials were filled to the top, without any headspace, and capped tightly. The foil-wrapped vials were incubated in that dark at 25°C. Three vials were sampled at 0, 2, 4, 9, 14, 21, and 28 days. Inorganic chloride in the solutions was quantitated with an ion-specific electrode, and chloropicrin was quantitated by gas chromatography with a flame ionization detector. In all solutions, final

chloropicrin concentrations were at least 90% of initial, and inorganic chloride never exceeded the detection limit of 1.5 mg/l.

Jeffers and Wolfe (1996) investigated chloropicrin hydrolysis at elevated temperatures (85 – 166°C) in aqueous 0.0003 μmol/l solutions sealed in Pyrex glass bulbs. Detectable hydrolysis occurred only at temperatures greater than 140°C, and Jeffers and Wolfe (1996) concluded that "homogeneous hydrolysis is a completely negligible process for chloropicrin." However, in another set of experiments, chloropicrin in an aqueous 0.0006 μmol/l solution was incubated with 0.5 g of an aquatic plant, parrot feather, and degraded via reduction to dichloronitromethane then chloride ion, with a half-life that was less than 20 hours. Jeffers and Wolfe (1996) concluded, based on this experiment and others with halogenated compounds, that "plant dehalogenases will degrade chloropicrin readily and completely, within 20 hours, as 'reasonable' concentrations."

Another study also reported a lack of hydrolysis in chloropicrin solutions incubated in the dark for 10 days (Moreno and Lee, 1993). This study is described below, in the Photohydrolysis section.

Photohydrolysis

Castro and Belser (1981) investigated hydrolysis of an aqueous, 0.01-M (1,640 mg/l) chloropicrin solution in a tube-shaped quartz photoreactor irradiated with a small, low-pressure quartz lamp at 254 nm. The photoreactor contained 100 ml solution and 115 ml headspace. Inorganic chloride was quantitated with an ion-specific electrode, chloropicrin was quantitated by gas chromatography with a flame ionization detector, nitrate was quantitated spectrophotometrically as nitrotoluene following reaction with toluene, and carbon dioxide was quantitated by gravimetric determination of barium carbonate after reaction with barium hydroxide. Following a 24-hour incubation at 25°C, no detectable chloropicrin remained in solution or in the headspace. Inorganic chloride was present at 0.003 M, nitrate at 0.00105 M, and carbon dioxide (in gas and solution) at 0.00097 M. Kinetics experiments with this apparatus showed that chloropicrin dissipated completely after 6 hours in light at 254 nm.

Additional kinetics experiments conducted by Castro and Belser (1981) investigated chloropicrin hydrolysis in solution under ambient light conditions, under a 150-watt flood lamp, and exposed to sunlight in a quartz cuvette in August. The latter two conditions yielded identical decay curves, with a half life of 3 days. Under ambient light, however, negligible hydrolysis occurred after 10 days. Castro and Belser (1981) concluded that photohydrolysis was proportional to the light available in the blue and ultraviolet regions of the electromagnetic spectrum. Furthermore, Castro and Belser (1981) concluded the fact that inorganic chloride was not formed at the expected rate of three times the disappearance of chloropicrin indicated the presence of chlorinated intermediates, which their analyses were not able to identify.

The hydrolysis of chloropicrin in a pH 7 aqueous 0.001-M solution was investigated by Moreno and Lee (1993); this study was also described by Wilhelm *et al.* (1996). Aliquots of the solution were injected with a syringe into 12-ml Teflon®-sealed vials, leaving no headspace, and incubated at 25°C under both dark and simulated-sunlight conditions (Suntest CPS photomachine with xenon lamp, 12-hour light/dark cycles). Three to five vials were sampled at 12, 24, 36, 48, 60, 72, 84 and 108 hours. Chloropicrin was quantitated by gas chromatography with a flame ionization detector, carbon dioxide was quantitated by gas chromatography/mass spectrometry, and a combination pH/ion analyzer was used to measure pH and to quantitate nitrate, nitrite, and chloride concentrations. There was no measurable hydrolysis of chloropicrin after 10 days under dark conditions. However, chloropicrin underwent significant photodegradation with simulated sunlight. The estimated half-life was 31.1 hours. After 10 days, the chloropicrin concentration had declined to 91% of its initial concentration. The degradation products identified included carbon dioxide (a portion of which would ionize in solution to bicarbonate at the pH tested), chloride, nitrate and nitrite.

Oxidation-Reduction Reactions

Under reducing conditions, chloropicrin undergoes a series of dechlorinations (Zheng *et al.*, 2006; Lee *et al*., 2008). To investigate reactions with reduced sulfur compounds, 50-ml aliquots of a deoxygenated 0.0005-M chloropicrin stock solution were mixed with a deoxygenated sulfide solution in 55-ml serum bottles capped with Teflon®-faced butyl rubber stoppers, and incubated in the dark at 25°C (Zheng *et al.*, 2006). Hydrolysis controls contained only chloropicrin solution. Chloropicrin was quantitated by gas chromatography with an electron capture detector, and transformation products were analyzed by gas chromatography/mass spectrometry. Chloropicrin reacted completely with the sulfide solution, and was non-detectable in less than 1 hour; decay was exponential. The reaction was increased more than 20-fold when pH was increased from 5.8 to 8.9. In contrast, no discernable hydrolysis occurred in the chloropicrin-only controls. Transformation products from the chloropicrin-sulfide reactions included dichloronitromethane and chloronitromethane. These products formed simultaneously in kinetics experiments, suggesting that the reactions involve formation of radicals. Zheng *et al.* (2006) suggest that such reactions may be a significant pathway for chloropicrin dissipation in the environment, especially after drip irrigation applications where the saturated soil becomes anoxic.

Laboratory experiments by Lee *et al.* (2008) suggest that reduced iron species, like the reduced sulfur species used by Zheng *et al.* (2006), quickly and quantitatively react with chloropicrin to form dichloronitromethane and nitromethane. In their study, Lee *et al.* (2008) determined the half-life of such reactions to be less than 5 minutes.

Chloropicrin as a Disinfection Byproduct in Drinking Water

In addition to its presence in water following pesticide applications, chloropicrin concentrations occur as a byproduct of reactions between organic matter and certain water treatment chemicals used in chlorination, as well as other oxidative treatments used to disinfect drinking water (Merlet *et al*., 1985). Chloropicrin is a minor disinfectant byproduct, as it is formed at a rate that is at least 10-fold slower than major byproducts such as

chloroform and is present in low concentrations (< 10 μg/L) under all conditions that have been investigated (Hoigné and Bader, 1988; Lee *et al.*, 2007; Yang *et al.*, 2007).

Chen and Weisel (1998) monitored several disinfection byproducts at three locations in a drinking water distribution system in New Jersey, in which free chlorine levels were maintained at 0.5 mg/L to prevent regrowth of microorganisms. Chloropicrin concentrations ranged from below the LOD of 0.05 μg/L to 0.9 μg/L. Mean chloropicrin concentrations were 0.1 μg/L in winter and 0.5 μg/L in summer. However, chloropicrin concentrations decreased with residence time in the distribution system, suggesting that chloropicrin was formed during treatment then dissipated following treatment; in contrast, most other byproducts continued to be formed during distribution of drinking water from the treatment plant (Chen and Weisel, 1998). Wells *et al.* (2001) found that grab samples of Seattle tap water contained chloropicrin at a mean concentration of 0.249 μg/L (n = 3), but that boiling tap water samples for 5 minutes decreased chloropicrin concentrations to below the LOD of 0.009 μg/L.

Krasner *et al.* (1989) collected quarterly water samples, from spring 1988 through winter 1989, at 35 utilities across the U.S. (ten of which were in California). These samples were analyzed for a number of disinfection byproducts, including chloropicrin. Results were reported as quarterly means across all 35 utilities; the quarterly mean for chloropicrin ranged 0.10 μg/L to 0.16 μg/L. Krasner *et al.* (1989) selected utilities operating under a wide variety of conditions. In a later study, Krasner *et al.* (2006) selected ten utilities with water sources high in organic carbon or bromide. Results were aggregated across all ten plants; the maximum chloropicrin concentration reported was 2.0 μg/L, and the median concentration was 0.2 μg/L.

Bioconcentration in Aquatic Organisms

Bioconcentration/bioaccumulation is defined by U.S. EPA (1996) as "the increase in concentration of the test substance in or on an organism (specified tissues thereof) relative to the concentration of test substance in the surrounding medium." Bioconcentration refers specifically to uptake of a substance solely from water. The bioconcentration factor (BCF) is the ratio of concentrations in fish tissues (expressed as wet weight of the fish) and surrounding water. A high BCF suggests a potential for a compound to segregate into body lipids rather than be excreted, and might be predicted from a high K_{ow} (Franke, 1996).

The relatively low K_{ow} and high water solubility of chloropicrin suggest that bioconcentration in aquatic organisms is likely to be low. Kenaga (1980) calculated a BCF of 8, based on a reported water solubility of 2,270 ppm. The calculation used a regression of BCF on water solubility for 170 chemicals. The regression equation was log BCF = 2.791 – 0.564(log water solubility).

Using the Estimation Program Interface, a software package available from U.S. EPA that relies on K_{ow} to predict the BCF, Sanderson *et al.* (2007) predicted a BCF of 8.1 for chloropicrin.

Persistence in Air Environment

Chloropicrin is reactive and has a relatively short half-life in air. Under laboratory conditions with simulated sunlight, chloropicrin vapor undergoes photodegradation to phosgene and nitrosyl chloride, with an estimated half-life of 18 hours under constant illumination in the laboratory (Carter *et al.*, 1997). Carter *et al.* (1997), citing reviews of atmospheric reactions of halogenated and nitro compounds by Atkinson (1989 and 1994), stated that the only significant reactions of chloropicrin in air are due to photolysis rather than reaction with radical species such as OH, ozone, and NO_3.

Photolysis

The photodegradation of chloropicrin in the vapor phase was analyzed by Moilanen *et al.* (1978) in the laboratory under simulated sunlight (275-W RS Sunlamp). Chloropicrin was vaporized in a photoreactor at 0.1, 1.4 and 14 g/ml and irradiated at sunlight wavelengths (> 290 nm) continuously for 70 days at 25°C – 30°C. Control flasks incubated at the same temperature but in the dark showed little chloropicrin loss over the 70-day study. The photodegradation half-life was 20 days for all concentrations. The initial photodegradation products were phosgene ($COCl_2$) and nitrosyl chloride (NOCl) resulting from the photochemical oxygenation of chloropicrin. Nitrosyl chloride underwent further degradation to nitric oxide (NO) and chlorine (Cl_2); the former oxidized further to yield nitrogen dioxide (NO_2). The accumulation of phosgene during the experiment indicated that it was relatively stable in the flasks under these experimental conditions.

Carter *et al.* (1997) measured chloropicrin absorption across the spectrum ranging 190 – 800 nm, and identified two maxima in the ranges 216 – 220 nm and 274 – 276 nm. Although Carter *et al.* (1997) observed no significant absorption at wavelengths above 370 nm, sufficient absorption occurred in the range 300 – 360 nm to suggest that photolysis will occur in ambient sunlight. Chloropicrin photodegradation was measured in a chamber with a xenon arc lamp. The half-life was estimated at 18 hours, and Carter *et al.* (1997) predicted that in ambient sunlight the half-life would range 3.4 – 7.6 hours; no data are available to test the prediction. However, these values are considerably less than the 20-day half-life reported by Moilenen *et al.* (1978), and are due to differences in light intensity at the locations of the spectrum where chloropicrin absorption occurs (Carter *et al*., 1997). Chloropicrin reactivity with several organic compounds was also monitored in the photoreactors. Chloropicrin reacted with the organic compounds, and catalyzed formation of ozone, but at a much slower rate than chlorine.

Wade *et al.* (2006) conducted detailed studies of chloropicrin photodissociation using a series of lamps and filters to specifically excite chloropicrin at wavelengths of 193 nm, 248 nm, and 266 nm. Emission spectra were monitored for chloropicrin in helium buffer gas using Fourier transform infrared emission spectroscopy. Wade *et al.* (2006) concluded that the primary response of chloropicrin to light at these wavelengths was to form a trichloromethyl radical and an electronically excited species of nitrogen dioxide:

$$CCl_3NO_2 \Rightarrow \bullet CCl_3 + NO_2^*$$

Both compounds rapidly react to form other products, such as nitric oxide. The evidence suggested that phosgene and nitrosyl chloride are secondary products of subsequent reactions.

EXPOSURE ASSESSMENT

Exposure estimates are provided for short-term (defined in this exposure assessment as acute and up to one week) and, where appropriate, for seasonal (intermediate-term intervals, lasting from one week to one year), annual, and lifetime exposures. Short-term exposures were estimated for 1-hour durations because chloropicrin irritation occurs rapidly, and 1 hour is the shortest duration for which toxicity endpoints and concentrations can reasonably be estimated. Short-term estimates of 8-hour and 24-hour durations are included to address occupational and residential exposures.

For short-term exposures, DPR estimates the highest exposure an individual may realistically experience during or following legal chloropicrin uses. To estimate seasonal, annual, and lifetime exposures, the average daily exposure is of interest because over these periods of time, a worker is expected to encounter a range of daily exposures (i.e., DPR assumes that with increased exposure duration, repeated daily exposure at the upper-bound level is unlikely). Typical exposure conditions are assumed for seasonal and annual exposure estimates. An annual exposure is a time-weighted average concentration that integrates use of chloropicrin throughout the year, and a lifetime exposure estimate averages daily exposure over a lifetime.

Bystander Exposure

Bystanders include individuals, working or not, who are not directly involved with a pesticide application but who may be exposed during or after the application by drift or volatilized pesticide. Bystanders are assumed to wear no protective clothing or equipment, such as that required for handlers of chloropicrin-containing products during an application. Occupational bystanders may be handling other pesticides or they may be doing fieldwork such as harvesting, and are assumed to be present next to the chloropicrin application for an 8-hour workday. Residential bystanders are assumed to be in the vicinity of the chloropicrin application for 24-hour days. This assumption covers individuals who may be unable to leave, for illness or other reason, and also protects individuals who are present for shorter intervals. While bystanders might potentially be exposed to a range of chloropicrin concentrations, for screening risk assessment purposes the highest realistic exposures to bystanders are reported in this exposure assessment.

Although buffer zones can be imposed on individual applications on a case-by-case basis, neither product labels nor state regulations impose consistent buffer zones on all chloropicrin uses. Consequently, individuals could be immediately adjacent to an application. However, exposure estimates for bystanders only assume that individuals can be as close as 10 ft (3 m) from the edge of a treated field during and following an application. For a 40-acre field, the difference in concentration between field edge and 3 m downwind is not expected to be

significant. Chloropicrin air concentrations were estimated at a point 1.2 m above ground, which is the assumed breathing zone.

Table 14 summarizes screening estimates of chloropicrin exposure of bystanders to soil fumigations. Short-term exposure estimates, including 1-hour, 8-hour, and 24-hour estimates, are concentrations taken from Table 9. A single product, Metapicrin (EPA Reg. No. 8622-43-AA), allows higher application rates of up to 1,076 lbs AI/acre (1,209 kg/ha) if followed by cultipacking or water seal. No other chloropicrin product allows applications at this rate. Short-term exposure estimates associated with applications of Metapicrin at this maximum rate are summarized in Appendix 2.

Table 14. Estimated Exposure of Bystanders to Chloropicrin from Soil Fumigation [a]

Duration	Concentration ($\mu g/m^3$)	Concentration (ppb)
1 Hour [b]	110,000	16,000
8 Hours [c]	44,000	6,500
24 Hours [d]	7,400	1,100
Seasonal [e]	490	73
Annual [f]	160	24
Lifetime [g]	70	10

[a] Reasonable worst case exposure estimates for bystanders were generated using the Industrial Complex Short Term, Version 3 (ISCST3) air dispersion model and flux data from application site monitoring studies in Arizona (Beard *et al*., 1996) and California (Rotondaro, 2004), adjusting for the maximum application rate and assuming the bystander was downwind, 10 ft (3.0 m) from the edge of a square, 40-acre field and the breathing zone was 1.2 m (4 ft) above ground (Barry, 2008a). Estimates have been rounded to 2 significant figures.

[b] The 1-hour exposure was estimated from the highest 6-hour concentration for the different application methods (using the peak-to-mean ratio: $C_p = C_m(t_p/t_m)^{½}$ where C_p is the peak concentration over the peak period of interest, t_p, and C_m is the mean concentration over mean measurement period, t_m.

[c] The highest 6-hour concentration was used for the 8-hour exposure. The 6-hour concentration was highest for broadcast non-tarped application at night.

[d] The 24-hour concentration was highest for the bedded tarped application.

[e] Seasonal exposure was estimated by calculating an average 24-hr flux over 2 weeks, then adjusted using a time-scaling factor based on the peak-to-mean theory (Barry, 2008c). Assumes a 4-month season.

[f] Annual average concentrations calculated as follows: Seasonal concentration x (4 months/12 months).

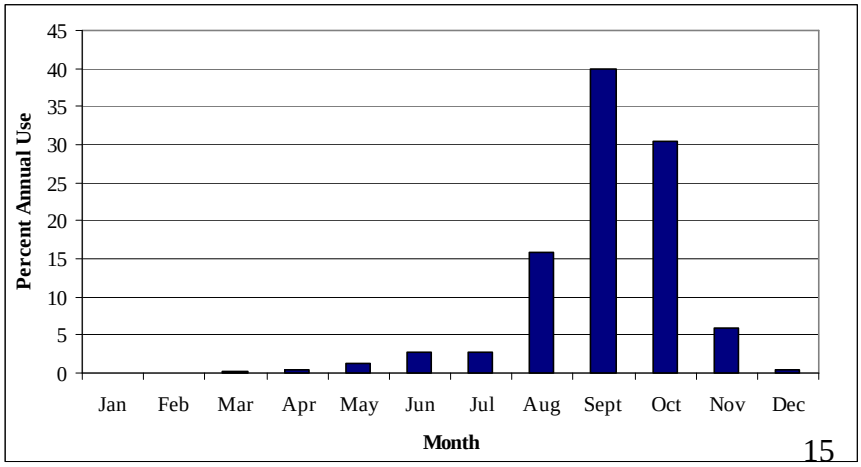
[g] Lifetime concentrations assume average annual exposures occur each year, adjusted for the 50th percentile application rate of 150 lbs AI/acre (168 kg AI/ha), over a lifetime for residential bystanders residing at the same location.

Seasonal, annual, and lifetime estimates are based on the highest 2-week concentration reported in Table 10. Surrogate data from the PUR were used to estimate intervals for seasonal and annual exposures. Chloropicrin is registered for pre-plant use for several different crops, and some crops with shorter growing seasons may be replanted multiple times a year, suggesting that bystanders in high-use areas may potentially be exposed throughout the year. However, PUR data show that in many parts of the state chloropicrin use does not occur throughout the year, and that at other times relatively few applications are made. It is reasonable to assume that an individual bystander is less likely to be exposed to chloropicrin

during these relatively low-use intervals. Thus, rather than assume that bystanders are exposed throughout the year, annual use patterns are plotted based on monthly PUR data from the county with the highest use. Annual exposure to chloropicrin is assumed to be limited to the months when use is relatively high (defined as 5% or more of annual use each month).

Figure 7 summarizes monthly applications of chloropicrin in Monterey County during the most recent 5 years available. Monterey County was selected because the highest use occurs in this county. Examination of Figure 7 shows that during each month between August and November, chloropicrin use was at least 5% of the annual total use, and that 92% of annual use occurred during these 4 months. Seasonal and annual exposure estimates assumed exposure durations of 4 months.

Figure 7. Applications of Chloropicrin in Monterey County, 2002 – 2006 [a]



[a] Percent calculations based on pounds applied (DPR, 2009; queried April 23, 2008).

For bystanders in active growing areas, such as in strawberry growing regions, exposures can potentially occur each year, as fields are fumigated before every crop. For a residential bystander with lifelong residency at the same location in one of these areas, average lifetime exposures would be expected to approximate annual exposures. However, as shown in Appendix 3 (Table A3-7), the application rate of 350 lbs AI/acre (393 kg AI/ha) that was assumed to be typical for annual exposure, is actually above the 95th percentile of all applications reported each year using 100% chloropicrin, suggesting that over a lifetime a bystander would be anticipated generally to be near applications at lower rates. Thus, the lifetime exposure estimate in Table 14 assumed the 50th percentile application rate of 150 lbs AI/acre (168 kg AI/ha) instead.

Table 15 summarizes screening estimates of chloropicrin exposure of bystanders to structural fumigations. Short-term exposure estimates, including 1-hour, 8-hour, and 24-hour, are concentrations taken from Table 13, and are all from the same study (ARB, 2005a). Data from studies monitoring structural fumigation suggest that chloropicrin dissipates quickly, and multiple structural fumigations are not anticipated in an area (Cochran and DiPaolo,

2006). Thus, seasonal, annual, and lifetime bystander exposures to chloropicrin from structural fumigation are not anticipated.

Table 15. Estimated Exposure of Bystanders to Chloropicrin from Structural Fumigation [a]

Duration	Concentration (μg/m^3)	Concentration (ppb)
1 Hour [b]	73	11
8 Hours [c]	16	2.4
24 Hours [d]	6.2	0.92

[a] Exposure estimates were based on the highest off-site concentrations measured during sulfuryl fluoride structural fumigation with chloropicrin as a warning agent in three studies conducted by the California Air Resources Board (ARB, 2003d; 2005a; 2005b). The study conducted in Nevada County during the fumigation of a two-story house with a fumigation volume of 81,000 ft^3 (2,300 m^3) had the highest air concentrations at a sampler 1.5 m northwest of the house during and following mechanical ventilation (ARB, 2005a). Concentrations were corrected for 79% field spike recovery and multiplied by 8/6 because the amount of chloropicrin used in monitoring study (6 oz; 180 ml) was below the maximum specified for warning agent use of 1 oz (30 ml) per 10,000 ft^3 (280 m^3) on the sulfuryl fluoride product label.

[b] The 1-hour exposure was based on the air concentration during the 1.6 hour sample.

[c] The 8-hour exposure was based on the time-weighted average of the consecutive 1.6 and 4.9-hour concentrations. Calculations shown in Table 13.

[d] The 24-hour exposure is based on the average of consecutive 12-hour concentrations.

Chloropicrin can be used to fumigate enclosed spaces; one product gives directions for its use as an AI in fumigating empty potato storages and empty grain bins. Table 16 summarizes screening exposure estimates for bystanders to enclosed space fumigation. In the absence of data specific to enclosed space fumigation, estimates were based on data from ARB (2005a), adjusted for maximum application rate (0.7 pounds (0.3 kg) per 1,000 ft^3 (28 m^3) and an estimated building size of 330,000 ft^3 (9,300 m^3), based on information from the University of California County Extension (Stoddard *et al.*, 2006; Stoddard, 2009). No chloropicrin use in storage areas has ever been reported in the PUR (DPR, 2009).

Enclosed space fumigation occurs between crops, and annual exposures were estimated assuming exposure of two days per year (assuming two crops per year). No seasonal exposures are anticipated: less than one week is considered a short-term exposure. Lifetime exposures assume average annual exposures occur each year over a lifetime for residential bystanders residing at the same location.

Indoor Air

The California Health and Safety Code Section 39660.5 requires that TAC assessments consider indoor air concentrations as well as ambient outdoor air. Members of the public can potentially be exposed to chloropicrin in indoor air if they enter a structure following fumigation. Two methyl bromide products containing chloropicrin, Metabrom 99 (EPA Reg. No. 8622-17-AA) and Methyl Bromide 99.5% (EPA Reg. No. 8536-12-ZA) have directions on the product label for structural fumigation. In addition, the sulfuryl product Vikane (EPA Reg. No. 62719-4-ZA) has directions for use of chloropicrin as a warning agent during

structural fumigation. Following fumigation with methyl bromide or sulfuryl fluoride, aeration is required until a certain level of fumigant AI is reached, but no monitoring of chloropicrin concentrations is required during or following fumigation.

Table 16. Estimated Exposure of Bystanders to Chloropicrin from Enclosed Space Fumigation [a]

Duration	Concentration (μg/m^3)	Concentration (ppb)
1 Hour [b]	2,400	360
8 Hours [c]	680	100
24 Hours [d]	210	31
Annual [e]	1.2	0.18
Lifetime [f]	1.2	0.18

[a] Exposure estimates were based on the highest off-site concentrations measured during sulfuryl fluoride structural fumigation with chloropicrin as a warning agent (ARB, 2005a). Concentrations were corrected for 79% field spike recovery and multiplied by 11 because the amount of chloropicrin used in monitoring study (6 oz; 180 ml) was below the maximum allowed for fumigating potato storage spaces of 0.7 pounds (0.3 kg) per 1,000 ft^3 (28 m^3), and the size structure monitored by ARB (2005a) was 81,000 ft^3 (2,300 m^3), vs. the size potato warehouse of 330,000 ft^3 (9,300 m^3) used in California (Stoddard *et al*., 2006).
[b] The 1-hour exposure was based on the air concentration during the 1.6 hour sample.
[c] The 8-hour exposure was based on the time-weighted average of the consecutive 1.6 and 4.9-hour concentrations. Calculations shown in Table 13.
[d] The 24-hour exposure is based on the average of consecutive 12-hour concentrations.
[e] Annual average concentrations calculated as follows: 24-hour concentration x (2 days/365 days).
[f] Lifetime concentrations assume average annual exposures occur each year over a lifetime for residential bystanders residing at the same location.

Air monitoring of structural fumigations conducted by ARB at DPR's request included two studies in which chloropicrin concentrations indoors were monitored with two 24-hour samples collected after completion of aeration (ARB, 2003d; 2005a). The indoor air concentrations associated the application monitored by ARB (2005a) were highest, and the indoor air exposure following structural fumigation are based on these data as summarized in Table 17.

Ambient Air

Air monitoring done at the request of DPR (ARB, 1987; 2003a; 2003b) suggests that airborne chloropicrin exposures not associated with particular applications can occur. Ambient air monitoring was done in three counties with relatively high use (Kern, Monterey, and Santa Cruz), during times when peak use was anticipated. Exposures to chloropicrin in ambient air are anticipated to be equal to or less than bystander exposures to chloropicrin, as the highest pesticide concentrations in air occur adjacent to an application (MacCollom *et al*., 1968; Siebers *et al*., 2003). Bystander exposure estimates are thus health-protective estimates for airborne chloropicrin exposures both adjacent to and away from applications.

Table 17. Estimated Indoor Air Exposure Chloropicrin Following Structural Fumigation

Duration [a]	Measured Concentration (μg/m^3)	Corrected [b] Concentration (μg/m^3)	Corrected [b] Concentration (ppb)
24 Hours	83	140	21

[a] Exposure estimate based on the highest indoor air concentrations measured post-aeration following a sulfuryl fluoride structural fumigation with chloropicrin as a warning agent in two studies conducted by the California Air Resources Board (ARB, 2003d; 2005a). The study conducted in Nevada County during the fumigation of a two-story house with a fumigation volume of 81,000 ft^3 had the highest air concentration during a 24-hour sample collected at an indoor sampler on the south end of the house following 16.5-hour aeration (ARB, 2005a).

[b] This concentration was corrected for 79% field spike recovery and multiplied by 8/6 because the amount of chloropicrin used in monitoring study (6 oz; 180 ml) was below the maximum specified for warning agent use of 1 oz (30 ml) per 10,000 ft^3 (280 m^3) on the sulfuryl fluoride product label.

EXPOSURE APPRAISAL

Exposure estimates for bystanders to soil fumigation were based on concentrations modeled from flux data. DPR used the ISCST3 air dispersion model, in screening mode, to develop deterministic estimates of off-site concentrations associated with soil fumigation (Barry, 2008a). This model uses the emission rate or flux, along with parameters including emission height, distance from the emission source, wind direction and speed, atmospheric stability (vertical mixing of heated air), the profile of temperature vs. height above ground, and urban or rural air dispersion patterns to estimate the downwind air concentrations (U.S. EPA, 1995). Flux data were available for multiple application methods, with most studies spanning several days. Monitoring included nighttime as well as daytime conditions, an important consideration as off-site concentrations are often highest during calm nighttime periods when peak fumigant emissions combine with atmospheric inversions (Segawa, 1997). Studies monitored flux during applications conducted in accordance with typical soil fumigation practices.

However, with the limited number of studies available, there is insufficient information available to determine how representative the chloropicrin flux measured in association with each application method might be. With the exception of broadcast tarped applications, none of the application methods have replicated data, which precludes estimating variability in the flux. Broadcast tarped applications were replicated three times, in Arizona, Washington, and Florida. The flux CVs of the three applications for different intervals (6-hour day, 6-hour night, and 24-hour) ranged from 48.8% - 116% (Appendix 1). The sources of variability are not known, but could include differences between applications in parameters that affect flux, including field size and shape, soil moisture, size and organic content of soil particles, and temperature. If the estimated flux is significantly greater or less than the true flux of chloropicrin, then concentrations calculated from the flux will be over- or underestimated from actual concentrations encountered by bystanders (Barry *et al.*, 2004). For broadcast tarped applications, estimates relied on data from the Arizona application, which had the highest flux of the three applications.

Although off-site concentrations were measured simultaneously with flux, bystander exposure estimates were not based on the off-site data. Not only might bystanders under different conditions of weather and atmospheric stability potentially be exposed to higher concentrations than were captured in the relatively few studies conducted, but bystanders might also be closer to an application than were samplers in these studies. DPR uses air-dispersion modeling to address limitations in the data and provide health-protective bystanders exposure estimates.

Modeling to determine off-site concentrations associated with soil fumigations incorporated various assumptions, each of which is associated with uncertainty. For example, one assumption was that the treated area is a square field, although DPR recognizes that treated areas can be rectangular or otherwise shaped. As explained by Barry *et al.* (2004), use of square fields provides a more consistent estimate "because the same centerline air concentrations will be obtained regardless of which side of the field the wind is blowing perpendicular over. This would not be the case if rectangular fields were used." It was further assumed that the treated area is 40 acres, as available information suggests that 40 acres is likely the maximum amount that can be treated in a single day by a single crew. A query of pesticide use in Monterey County suggests that in a recent 5-year period, between 1.5% and 5.5% of applications each year reported treating more than 40 acres (DPR, 2009; data not shown). However, PUR reports can collapse multiple-day applications into a single day, and it is likely that not all of these applications actually treated more than 40 acres in one day (e.g., one application reported treating more than 500 acres). If a larger area is treated by using more than one crew, then the off-site concentration would be anticipated to be higher than estimated.

Short-term off-site concentrations associated with soil fumigations were adjusted to account for differences between the application rates monitored in flux studies and the maximum allowed application rate for chloropicrin. DPR believes upper-bound estimates are appropriate for short-term exposures because high-end exposures are possible, and DPR has an obligation to protect all individuals exposed to pesticides as a result of legal uses. Protecting at the level of "average or typical" exposure would, by definition, suggest that many individuals (anyone with above-average exposure) could be exposed to acutely toxic concentrations. In contrast, for seasonal and annual exposures, DPR believes that assumption of more typical exposure conditions is appropriate. Thus, seasonal and annual bystander exposure estimates assume that application rates on average do not exceed 350 lbs AI/acre. This specific rate was chosen because it is supported by registrants and because it was the maximum soil fumigation rate assumed in the U.S. EPA human health risk assessment (Reaves and Smith, 2008). That is, this rate is generally agreed to be a reasonable rate. Furthermore, examination of applications made during a recent 5-year interval (2002 – 2006) in the ten counties with the highest chloropicrin use suggest that applications at rates higher than 350 lbs AI/acre are relatively rare, less than 0.1% of all applications (DPR, 2009; data not shown).

Concentration adjustments for various application rates assume that flux is a constant proportion of the application rate, and that concentrations are directly proportional to flux. Some uncertainty is associated with these adjustments, particularly as the estimates involve higher application rates than were used in the flux studies. With respect to such adjustments, Barry *et al.* (2004) noted that, "It is likely that due to the same or greater soil adsorption and degradation, the flux proportion is the same or less for application rates lower than those monitored. It is not known whether the flux increases proportionally with application rate for rates beyond those monitored."

Sampling intervals during soil fumigations generally ranged 6-24 hours. Over shorter intervals, higher concentrations can occur as the plume meanders (Csanady, 1973; Pasquill, 1974). As available information suggests that shorter exposures to chloropicrin can result in adverse effects, 1-hour concentrations were estimated by using peak-to-mean ratio techniques to adjust 6-hour concentrations (Barry, 2000). Peak-to-mean calculations are based on the premise that the mean concentration during a longer interval averages a series of peaks, and that shorter intervals will tend to have higher peaks; thus the concentration measured during the longer interval can be adjusted by a factor that incorporates the square root of the ratio of durations of the longer and shorter intervals (O'Malley *et al.*, 2004b).

Seasonal, annual, and lifetime exposure estimates associated with soil fumigations are based on a 2-week concentration for a bystander adjacent to a single application. The 4-month interval for seasonal and annual exposure assumes a bystander is exposed to airborne chloropicrin from multiple applications during the high-use season, occurring 2 weeks apart. Soil fumigation is done before crops are planted. Generally, a single application is made prior to planting; however, a second fumigation is possible. For example, two fumigations 2 weeks apart are recommended to control nematodes in walnut orchard areas (McKenry and Westerdahl, 2007). The PUR data do not report if a field is treated only once or more than once.

The likelihood of multiple soil fumigations near a bystander is supported by the frequency of applications in some sections of Monterey County. For example, in one section chloropicrin applications to strawberries were reported 22 – 38 days each year, over 4-month intervals, in the years 2002 – 2006 (DPR, 2009; data not shown). The 1-mi^2 (259-hectare) sections are the smallest increment in which PUR data are reported (Wilhoite *et al.*, 2001). Not all of these applications would be adjacent to a single location, but a single location could be in the same section as all of the applications. In the absence of information with greater spatial resolution, 4 months duration for seasonal and annual exposures is considered a reasonable yet health-protective assumption.

Concentrations estimated from modeling can be compared to concentrations found in off-site monitoring. For short-term durations, Table 7 summarizes measured off-site concentrations adjusted for maximum application rate. These concentrations can be compared to concentrations obtained through modeling and summarized in Table 9. For example, the highest concentration following a broadcast non-tarped application, adjusted for the maximum application rate, was 5,322 $\mu g/m^3$ occurring during a 6-hour sample and reported in

Table 7. In Table 9, the comparable concentrations are 7,500 μg/m^3 and 44,000 μg/m^3, for 6-hour day and night intervals, respectively. It is unlikely that the highest possible concentrations for an application method would be measured in any given study, and it's not surprising that concentrations in Table 9 are higher than those in Table 7. Yet, the modeling-based estimates are within an order of magnitude of measured concentrations, which does not represent an extreme difference given the variability of concentrations measured within each study and given that off-site samplers were further from the edge of the field than the distance assumed by the modeling-based estimates. At least two other factors are anticipated to substantially contribute to differences between modeled and measured concentrations: weather conditions were likely different during study sampling intervals than the conditions assumed during modeling to obtain reasonable worst-case estimates, and modeled concentrations assumed a 40-acre field, while monitored fields receiving applications ranged 5.92 – 8.67 acres, or 4.6- to 6.8-fold smaller. For two fields treated at the same application rate, a greater amount of material is emitted from the larger field, increasing downwind concentrations (Barry, 2005b; Reaves and Smith, 2008).

Off-site chloropicrin concentrations and exposure estimates were lower for bystanders to structural fumigations than for bystanders to soil fumigations. Smaller amounts of chloropicrin are used with structural fumigations, both because of the smaller unit being treated and because chloropicrin is only used as a warning agent for structural fumigations. The largest application monitored, involving a 81,000-ft^3 (2,300-m^3) structure, also yielded the highest concentration measured in association with any of the three structural fumigations monitored. The highest concentration occurred at a sampler, labeled NWI, positioned 5 feet (1.5 m) from one edge of the structure, during a 1.5-hour aeration interval (ARB, 2005a). Furthermore, samplers positioned on the other side of the house from the NWI sampler had chloropicrin results that were all below the LOQ during all monitoring intervals, suggesting that sampler NWI was consistently downwind of the application. Unlike bystander exposure estimates associated with soil fumigation, which were calculated using air dispersion modeling for the reasons previously stated, bystander exposures associated with structural fumigation were based on measured off-site concentrations. As the sampler was approximately as close to the structure as the nearest likely bystander, and as the off-site chloropicrin concentrations quickly decreased following aeration (no samples contained chloropicrin greater than the LOQ after the samples collected 6 hours post-aeration), measured off-site concentrations are anticipated to be health-protective.

Off-site concentrations associated with structural fumigation were corrected for field spike recoveries and adjusted for maximum allowed application rate, but not for application size. The largest structure for which data are available was the two-story house described by ARB (2005a) as having an estimated volume of 81,000-ft^3 (2,300-m^3). Assuming each story is 10 feet (2.5 m) high, the house size is 4,050 ft^2 (376 m^2). This is on the larger end of houses in California; the national median house size was estimated at 1,769 ft^2 (164 m^2) in 2007 (U.S. Census Bureau, 2008). Although larger homes could be fumigated, they are likely to be located on larger properties, suggesting that bystanders might be expected to be farther from the application than with smaller homes in more closely-packed neighborhoods. Presently, no

data are available to assess how representative the application monitored by ARB (2005a) is of an upper-bound exposure to bystanders.

Indoor air exposures to chloropicrin were estimated for individuals entering structures following fumigation and aeration. Exposure estimates were based on 24-hour TWA sampling conducted by ARB following structural fumigation with sulfuryl fluoride as an AI and chloropicrin as a warning agent. Sequential 24-hour samples yielded lower concentrations in the second set of samples (collected 24 – 48 hours post-aeration) than the first set collected during the first 24 hours post-aeration, suggesting that concentrations continued to decrease following aeration. If the initial sampling interval were shorter than 24 hours, the indoor concentration might be anticipated to be higher.

No phosgene monitoring has been done in conjunction with any chloropicrin application. Under laboratory conditions with simulated sunlight, chloropicrin vapor undergoes photodegradation to phosgene and nitrosyl chloride, with an estimated half-life of 18 hours under constant illumination in the laboratory (Carter *et al.*, 1997). As part of its data call-in for chloropicrin, DPR requested information on whether the photodegradation product phosgene should be monitored as part of the air monitoring studies (Jones, 2002). In response, Gills *et al.* (2002) reviewed the literature on chloropicrin photolysis and estimated air concentrations of phosgene based on computer modeling. Gills *et al.* (2002) concluded that under field conditions chloropicrin degradation products, including phosgene, would remain below levels of concern. DPR staff in the Environmental Monitoring Branch reviewed the submission by Gills *et al.* (2002), and agreed with its general conclusions (Barry and Segawa, 2002). Subsequently, DPR decided that air monitoring should focus on the primary irritant, chloropicrin.

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APPENDIX 1. COEFFICIENT OF VARIATION FOR CHLOROPICRIN FLUX FROM BROADCAST TARPED APPLICATIONS

Table A1-1. Coefficient of Variation for Chloropicrin Flux from Broadcast Tarped Applications [a]

Sampling Interval [b]	Flux (μg/m^2/sec) [c]	Study Application Rate (lbs/Acre)	Flux Adjusted to Maximum Application Rate of 350 lbs AI/acre (μg/m^2/sec) [d]
6-Hour Day			
Arizona	132	332	139
Washington	70	343	71
Florida	58	346	59
Mean			90
Standard Deviation			43.3
Coefficient of Variation [e]			**48.8 %**
6-Hour Night			
Arizona	142	332	150
Washington	20	343	20
Florida	22	346	22
Mean			64
Standard Deviation			74.1
Coefficient of Variation			**116 %**
24-Hour			
Arizona	108	332	114
Washington	34	343	35
Florida	28	346	28
Mean			59
Standard Deviation			47.6
Coefficient of Variation			**80.8 %**

[a] From Barry (2008a), based on data from Beard *et al.* (1996). Flux estimates were generated with the Industrial Source Complex Short Term Version 3 (ISCST3) air dispersion model.

[b] The flux values for 1-hour day and night intervals were calculated from the corresponding 6-hour intervals, and would have the same coefficient of variation as the 6-hour flux values.

[c] The reported flux is the highest flux value obtained using the study flux profiles; a rolling average method was used to obtain the highest flux for each 24-hour interval when sampling intervals were less than 24 hours (Barry, 2008a).

[d] This rate is the maximum broadcast tarped application rate allowed on any chloropicrin product label currently registered in California.

[e] Coefficient of variation calculated as follows: 100% x (standard deviation)/(mean)

APPENDIX 2. OFF-SITE SHORT-TERM CHLOROPICRIN CONCENTRATIONS AND EXPOSURE ESTIMATES FOR METAPICRIN

Table A2-1. Chloropicrin Off-Site Air Concentrations Estimated for Metapicrin at the Maximum Application Rate and a Distance of 10 Feet (3.0 Meters) from the Edge of the Field [a]

Application Method	Application Rate (lbs/Acre) [b]	1-Hour, Day ($\mu g/m^3$)	1-Hour, Night ($\mu g/m^3$)	6-Hour, Day ($\mu g/m^3$)	6-Hour, Night ($\mu g/m^3$)	24-Hour ($\mu g/m^3$)
Broadcast non-tarped	1,076 [c]	39,000	**240,000**	16,000	**95,000**	**14,000**
Bedded non-tarped	538 [c]	90,000	140,000	37,000	58,000	11,000
Bedded tarped	500	44,000	77,000	18,000	31,000	7,600
Broadcast tarped	500	40,000	9,300	16,000	3,800	4,200
Bedded drip tarped	300	11,000	2,100	4,700	840	1,100

[a] From Barry (2008c), based on data from Beard *et al.* (1996), except for bedded drip tarp by Rotondaro (2004). Concentrations were generated with the Industrial Source Complex Short Term Version 3 (ISCST3) air dispersion model, and have been rounded to two significant figures. Bolded values represent the highest concentration for each interval. The concentrations assumed a receptor 1.2 m above ground and 10 ft (3.0 m) from the edge of a square, 40-acre (16-ha) treated area. Multiply value by 0.1487 to get result in parts per billion (ppb).

[b] Rate in pounds of chloropicrin per acre (lbs/acre), also referred to as pounds active ingredient per acre (lbs AI/acre). Multiply value by 1.123 to get rate in kilograms per hectare (kg/ha).

[c] Product labels for Metapicrin (EPA Reg. No. 8622-43-AA) allow a maximum application rate of 1,076 lbs AI/acre (1,209 kg/ha) for shank fumigations sealed by cultipacking or water seal. The rates for tarped applications are that same as rates on other chloropicrin product labels.

Table A2-2. Estimated Short-Term Exposure of Bystanders to Chloropicrin from Soil Fumigation with Metapicrin [a]

Duration	Concentration ($\mu g/m^3$) [b]	Concentration (ppb) [b]
1 Hour	240,000	36,000
8 Hours	95,000	14,000
24 Hours	14,000	2,100

[a] Estimates were based on modeling and direct flux measurements, and have been rounded to 2 significant figures. Product labels for Metapicrin (EPA Reg. No. 8622-43-AA) allow a maximum application rate of 1,076 lbs AI/acre (1,209 kg/ha) for shank fumigations sealed by cultipacking or water seal. Exposure estimates assume this rate.

[b] 1-Hour, 8-hour, and 24-hour concentrations from Table A2-1.

APPENDIX 3. OFF-SITE SHORT-TERM CHLOROPICRIN CONCENTRATIONS ESTIMATED FOR SUBMAXIMUM APPLICATION RATES

Screening estimates are provided in the exposure assessment. These reasonable worst-case exposure estimates are intended to address exposures associated with all legal uses. Risk managers and others might be interested in additional exposures estimated under conditions of lower application rates, longer distances away from an application, and smaller applications (fewer acres treated). The tables in this appendix provide selected estimates for each of five application methods.

Table A3-1. Chloropicrin Off-Site Air Concentrations Estimated for Broadcast Non-Tarped Applications to a 40-Acre Square Field [a]

Distance from Edge of 40-Acre Square Field	Application Rate (lbs/Acre) [b]	1-Hour, Day (μg/m^3)	1-Hour, Night (μg/m^3)	6-Hour, Day (μg/m^3)	6-Hour, Night (μg/m^3)	24-Hour (μg/m^3)
Current Maximum [c]						
10 feet (3.0 meters)	500	18,000	110,000	7,500	44,000	6,500
50 feet (15 meters)	500	17,000	110,000	7,000	44,000	5,900
100 feet (30 meters)	500	16,000	100,000	6,400	42,000	5,100
300 feet (91 meters)	500	11,000	83,000	4,600	34,000	3,400
500 feet (152 meters)	500	9,100	69,000	3,700	28,000	2,700
1,320 feet (402 meters)	500	5,500	44,000	2,200	18,000	1,500
2,500 feet (760 meters)	500	3,700	31,000	1,500	13,000	950
CMTF [d]						
10 feet (3.0 meters)	175	6,400	38,000	2,600	15,000	2,300
50 feet (15 meters)	175	6,000	37,000	2,500	15,000	2,100
100 feet (30 meters)	175	5,500	36,000	2,300	15,000	1,800
300 feet (91 meters)	175	3,900	29,000	1,600	12,000	1,200
500 feet (152 meters)	175	3,200	24,000	1,300	9,900	950
1,320 feet (402 meters)	175	1,900	15,000	780	6,200	540
2,500 feet (760 meters)	175	1,300	11,000	530	4,400	330

[a] From Barry (2008a), based on data from Beard *et al.* (1996), except for bedded drip tarp by Rotondaro (2004). Concentrations were generated with the Industrial Source Complex Short Term Version 3 (ISCST3) air dispersion model, and have been rounded to two significant figures. The concentrations assumed a receptor 1.2 m above ground and 10 ft (3.0 m) from the edge of a square, 40-acre (16-ha) treated area. Multiply value by 0.1487 to get result in parts per billion (ppb).

[b] Multiply value by 1.123 to get rate in kilograms per hectare (kg/ha).

[c] This application rate is the maximum allowed for that method on any product label currently registered in California.

[d] Application rate proposed for this use by the Chloropicrin Manufacturers Task Force, and assumed in U.S. EPA final revised human health risk assessment (Reaves and Smith, 2008). Concentrations corresponding to these rates are informational only, as (with the exception of bedded drip tarped applications) current product labels exceed these rates.

Table A3-2. Chloropicrin Off-Site Air Concentrations Estimated for Bedded Non-Tarped Applications to a 40-Acre Square Field [a]

Distance from Edge of 40-Acre Square Field	Application Rate (lbs/Acre) [b]	1-Hour, Day ($\mu g/m^3$)	1-Hour, Night ($\mu g/m^3$)	6-Hour, Day ($\mu g/m^3$)	6-Hour, Night ($\mu g/m^3$)	24-Hour ($\mu g/m^3$)
Current Maximum [c]						
10 feet (3.0 meters)	250	42,000	67,000	17,000	27,000	5,000
50 feet (15 meters)	250	39,000	67,000	16,000	27,000	4,500
100 feet (30 meters)	250	36,000	65,000	15,000	26,000	3,900
300 feet (91 meters)	250	26,000	52,000	11,000	21,000	2,600
500 feet (152 meters)	250	21,000	43,000	8,500	18,000	2,100
1,320 feet (402 meters)	250	13,000	27,000	5,100	11,000	1,200
2,500 feet (760 meters)	250	8,500	19,000	3,500	7,800	730
CMTF [d]						
10 feet (3.0 meters)	175	29,000	47,000	12,000	19,000	3,500
50 feet (15 meters)	175	28,000	47,000	11,000	19,000	3,200
100 feet (30 meters)	175	25,000	45,000	10,000	18,000	2,700
300 feet (91 meters)	175	18,000	36,000	7,400	15,000	1,900
500 feet (152 meters)	175	15,000	30,000	5,900	12,000	1,500
1,320 feet (402 meters)	175	8,800	19,000	3,600	7,700	830
2,500 feet (760 meters)	175	5,900	13,000	2,400	5,500	510

[a] From Barry (2008a), based on data from Beard *et al*. (1996), except for bedded drip tarp by Rotondaro (2004). Concentrations were generated with the Industrial Source Complex Short Term Version 3 (ISCST3) air dispersion model, and have been rounded to two significant figures. The concentrations assumed a receptor 1.2 m above ground and 10 ft (3.0 m) from the edge of a square, 40-acre (16-ha) treated area. Multiply value by 0.1487 to get result in parts per billion (ppb).

[b] Multiply value by 1.123 to get rate in kilograms per hectare (kg/ha).

[c] This application rate is the maximum allowed for that method on any product label currently registered in California.

[d] Application rate proposed for this use by the Chloropicrin Manufacturers Task Force, and assumed in U.S. EPA final revised human health risk assessment (Reaves and Smith, 2008). Concentrations corresponding to these rates are informational only, as (with the exception of bedded drip tarped applications) current product labels exceed these rates.

Table A3-3. Chloropicrin Off-Site Air Concentrations Estimated for Bedded Tarped Applications to a 40-Acre Square Field [a]

Distance from Edge of 40-Acre Square Field	Application Rate (lbs/Acre) [b]	1-Hour, Day ($\mu g/m^3$)	1-Hour, Night ($\mu g/m^3$)	6-Hour, Day ($\mu g/m^3$)	6-Hour, Night ($\mu g/m^3$)	24-Hour ($\mu g/m^3$)
Current Maximum [c]						
10 feet (3.0 meters)	500	44,000	77,000	18,000	31,000	7,400
50 feet (15 meters)	500	41,000	76,000	17,000	31,000	6,700
100 feet (30 meters)	500	38,000	74,000	15,000	30,000	5,700
300 feet (91 meters)	500	27,000	59,000	11,000	24,000	3,900
500 feet (152 meters)	500	22,000	49,000	8,900	20,000	3,100
1,320 feet (402 meters)	500	13,000	31,000	5,400	13,000	1,700
2,500 feet (760 meters)	500	8,900	22,000	3,600	8,900	1,100
CMTF [d]						
10 feet (3.0 meters)	350	31,000	54,000	13,000	22,000	5,200
50 feet (15 meters)	350	29,000	53,000	12,000	22,000	4,700
100 feet (30 meters)	350	27,000	52,000	11,000	21,000	4,000
300 feet (91 meters)	350	19,000	41,000	7,800	17,000	2,700
500 feet (152 meters)	350	15,000	34,000	6,200	14,000	2,200
1,320 feet (402 meters)	350	9,200	22,000	3,800	8,900	1,200
2,500 feet (760 meters)	350	6,200	15,000	2,500	6,300	760

[a] From Barry (2008a), based on data from Beard *et al*. (1996), except for bedded drip tarp by Rotondaro (2004). Concentrations were generated with the Industrial Source Complex Short Term Version 3 (ISCST3) air dispersion model, and have been rounded to two significant figures. The concentrations assumed a receptor 1.2 m above ground and 10 ft (3.0 m) from the edge of a square, 40-acre (16-ha) treated area. Multiply value by 0.1487 to get result in parts per billion (ppb).

[b] Multiply value by 1.123 to get rate in kilograms per hectare (kg/ha).

[c] This application rate is the maximum allowed for that method on any product label currently registered in California.

[d] Application rate proposed for this use by the Chloropicrin Manufacturers Task Force, and assumed in U.S. EPA final revised human health risk assessment (Reaves and Smith, 2008). Concentrations corresponding to these rates are informational only, as (with the exception of bedded drip tarped applications) current product labels exceed these rates.

Table A3-4. Chloropicrin Off-Site Air Concentrations Estimated for Broadcast Tarped Applications to a 40-Acre Square Field [a]

Distance from Edge of 40-Acre Square Field	Application Rate (lbs/Acre) [b]	1-Hour, Day ($\mu g/m^3$)	1-Hour, Night ($\mu g/m^3$)	6-Hour, Day ($\mu g/m^3$)	6-Hour, Night ($\mu g/m^3$)	24-Hour ($\mu g/m^3$)
Current Maximum [c]						
10 feet (3.0 meters)	500	40,000	9,300	16,000	3,800	4,300
50 feet (15 meters)	500	38,000	9,200	15,000	3,800	3,900
100 feet (30 meters)	500	35,000	9,000	14,000	3,700	3,400
300 feet (91 meters)	500	25,000	7,100	10,000	2,900	2,300
500 feet (152 meters)	500	20,000	5,900	8,100	2,400	1,800
1,320 feet (402 meters)	500	12,000	3,700	4,900	1,500	1,000
2,500 feet (760 meters)	500	8,100	2,600	3,300	1,100	630
CMTF [d]						
10 feet (3.0 meters)	350	28,000	6,500	12,000	2,600	3,000
50 feet (15 meters)	350	26,000	6,500	11,000	2,600	2,700
100 feet (30 meters)	350	24,000	6,300	10,000	2,600	2,400
300 feet (91 meters)	350	17,000	5,000	7,100	2,000	1,600
500 feet (152 meters)	350	14,000	4,200	5,700	1,700	1,300
1,320 feet (402 meters)	350	8,400	2,600	3,400	1,100	720
2,500 feet (760 meters)	350	5,700	1,900	2,300	760	440

[a] From Barry (2008a), based on data from Beard *et al*. (1996), except for bedded drip tarp by Rotondaro (2004). Concentrations were generated with the Industrial Source Complex Short Term Version 3 (ISCST3) air dispersion model, and have been rounded to two significant figures. The concentrations assumed a receptor 1.2 m above ground and 10 ft (3.0 m) from the edge of a square, 40-acre (16-ha) treated area. Multiply value by 0.1487 to get result in parts per billion (ppb).

[b] Multiply value by 1.123 to get rate in kilograms per hectare (kg/ha).

[c] This application rate is the maximum allowed for that method on any product label currently registered in California.

[d] Application rate proposed for this use by the Chloropicrin Manufacturers Task Force, and assumed in U.S. EPA final revised human health risk assessment (Reaves and Smith, 2008). Concentrations corresponding to these rates are informational only, as (with the exception of bedded drip tarped applications) current product labels exceed these rates.

Table A3-5. Chloropicrin Off-Site Air Concentrations Estimated for Bedded Drip Tarped Applications to a 40-Acre Square Field [a]

Distance from Edge of 40-Acre Square Field	Application Rate (lbs/Acre) [b]	1-Hour, Day ($\mu g/m^3$)	1-Hour, Night ($\mu g/m^3$)	6-Hour, Day ($\mu g/m^3$)	6-Hour, Night ($\mu g/m^3$)	24-Hour ($\mu g/m^3$)
Current Maximum [c]						
10 feet (3.0 meters)	300	11,000	2,100	4,700	840	1,100
50 feet (15 meters)	300	11,000	2,000	4,300	840	1,000
100 feet (30 meters)	300	9,800	2,000	4,000	810	860
300 feet (91 meters)	300	7,000	1,600	2,900	650	590
500 feet (152 meters)	300	5,600	1,300	2,300	540	460
1,320 feet (402 meters)	300	3,400	830	1,400	340	260
2,500 feet (760 meters)	300	2,300	590	940	240	160
CMTF [d]						
10 feet (3.0 meters)	300	11,000	2,100	4,700	840	1,100
50 feet (15 meters)	300	11,000	2,000	4,300	840	1,000
100 feet (30 meters)	300	9,800	2,000	4,000	810	860
300 feet (91 meters)	300	7,000	1,600	2,900	650	590
500 feet (152 meters)	300	5,600	1,300	2,300	540	460
1,320 feet (402 meters)	300	3,400	830	1,400	340	260
2,500 feet (760 meters)	300	2,300	590	940	240	160

[a] From Barry (2008a), based on data from Beard *et al*. (1996), except for bedded drip tarp by Rotondaro (2004). Concentrations were generated with the Industrial Source Complex Short Term Version 3 (ISCST3) air dispersion model, and have been rounded to two significant figures. The concentrations assumed a receptor 1.2 m above ground and 10 ft (3.0 m) from the edge of a square, 40-acre (16-ha) treated area. Multiply value by 0.1487 to get result in parts per billion (ppb).

[b] Multiply value by 1.123 to get rate in kilograms per hectare (kg/ha).

[c] This application rate is the maximum allowed for that method on any product label currently registered in California.

[d] Application rate proposed for this use by the Chloropicrin Manufacturers Task Force, and assumed in U.S. EPA final revised human health risk assessment (Reaves and Smith, 2008). Concentrations corresponding to these rates are informational only, as (with the exception of bedded drip tarped applications) current product labels exceed these rates.

Previous tables in this appendix summarize concentrations associated with applications to 40 acres, approximately the maximum that can be treated with a single application rig in one day. The next two tables summarize chloropicrin applications reported over a recent 5-year interval. Only applications of products containing 94 – 100% chloropicrin are included, as screening estimates are based on these products. Following the next two tables, subsequent tables report estimated concentrations associated with applications at the 50th percentile in size (number of acres treated) and application rate.

Table A3-6. Chloropicrin Application Sizes Using Chloropicrin-Only Formulations [a]

Year	N [b]	Acres Treated (Percentile) [c]						
		10th	25th	50th	75th	90th	95th	100th [d]
2003	336	1.5	5.0	12.2	22.0	59.1	79.0	277
2004	237	2.0	6.5	15.9	28.0	70.0	87.2	255
2005	281	2.4	5.0	12.0	23.8	46.0	80.0	155
2006	221	2.5	5.0	13.0	27.0	48.0	73.7	265
2007	220	2.3	7.8	15.5	33.0	77.0	110	263
5-year aggregate	1,295	2.1	5.4	13.7	27.0	58.2	84.3	277

[a] Applications in California, reported as acres treated, using products containing 94 – 100% chloropicrin (DPR, 2009; queried on multiple dates between January 29, 2009 and February 3, 2009).
[b] Number of applications reported in each year, and over all five years.
[c] Calculated with PERCENTILE function in Microsoft Excel.
[d] Application sizes above 120 acres or so are likely to have spanned multiple days. Some smaller applications might also have occurred over multiple days as well.

Table A3-7. Chloropicrin Application Rates Using Chloropicrin-Only Formulations [a]

Year	N [b]	Application Rate in Lbs AI/acre (Percentile) [c]						
		10th	25th	50th	75th	90th	95th	100th
2003	336	50.0	94.0	188	198	207	235	800
2004	237	49.9	75.2	148	200	205	212	372
2005	281	21.0	59.4	111	188	204	218	398
2006	221	5.4	45.5	113	168	198	200	255
2007	220	51.5	75.2	149	188	199	203	498
5-year aggregate	1,295	39.6	68.3	141	198	203	212	800

[a] Applications in California, reported as acres treated, using products containing 94 – 100% chloropicrin (DPR, 2009; queried on multiple dates between January 29, 2009 and February 3, 2009). Applications are in pounds chloropicrin per acre.
[b] Number of applications reported in each year, and over all five years.
[c] Application rates reported in pounds active ingredient per acre (lbs AI/acre), calculated with PERCENTILE function in Microsoft Excel.

Applications reported in the PUR do not include information about whether they are broadcast or bedded, or whether they are tarped or non-tarped. Furthermore, sizes of bedded applications might be reported as bedded acres, or as the entire field including beds and furrows; possibly some bedded applications are reported each way. Because of these limitations, it is not possible to estimate application rates at a particular (e.g., 50th) percentile for individual application methods. The following tables in this appendix all report off-site concentrations for an assumed 50th percentile application, with the same application size (15 acres) and effective broadcast application rate (150 lbs AI/acre), regardless of application method.

Table A3-8. Chloropicrin Off-Site Air Concentrations Estimated for Broadcast Non-Tarped Applications to a 15-Acre Square Field [a]

Distance from Edge of 15-Acre Square Field	Application Rate (lbs/Acre) [b]	1-Hour, Day ($\mu g/m^3$)	1-Hour, Night ($\mu g/m^3$)	6-Hour, Day ($\mu g/m^3$)	6-Hour, Night ($\mu g/m^3$)	24-Hour ($\mu g/m^3$)
Current Maximum [c]						
10 feet (3.0 meters)	500	15,000	79,000	6,000	32,000	5,500
50 feet (15 meters)	500	14,000	81,000 [d]	5,800	33,000 [d]	4,900
100 feet (30 meters)	500	13,000	79,000	5,100	32,000	4,100
300 feet (91 meters)	500	8,500	61,000	3,500	25,000	2,600
500 feet (152 meters)	500	6,600	49,000	2,700	20,000	2,000
1,320 feet (402 meters)	500	3,700	29,000	1,500	12,000	1,000
2,500 feet (760 meters)	500	2,300	20,000	940	8,100	530
50th Percentile [e]						
10 feet (3.0 meters)	150	4,400	24,000	1,800	9,700	1,600
50 feet (15 meters)	150	4,300	24,000	1,700	10,000 [d]	1,500
100 feet (30 meters)	150	3,800	24,000	1,500	9,700	1,200
300 feet (91 meters)	150	2,500	18,000	1,000	7,500	790
500 feet (152 meters)	150	2,000	15,000	800	6,000	600
1,320 feet (402 meters)	150	1,100	8,800	450	3,600	310
2,500 feet (760 meters)	150	690	5,900	280	2,400	160

[a] From Barry (2009), based on data from Beard *et al*. (1996), except for bedded drip tarp by Rotondaro (2004). Concentrations were generated with the Industrial Source Complex Short Term Version 3 (ISCST3) air dispersion model, and have been rounded to two significant figures. The concentrations assumed a receptor 1.2 m above ground and 10 ft (3.0 m) from the edge of a square, 15-acre (6.1-ha) treated area. Multiply value by 0.1487 to get result in parts per billion (ppb).

[b] Multiply value by 1.123 to get rate in kilograms per hectare (kg/ha).

[c] This application rate is the maximum allowed for that method on any product label currently registered in California.

[d] In some cases concentrations are lower at 10 ft than at 50 ft because concentrations are estimated in the breathing zone rather than at ground level. A the field edge, concentrations are higher at ground level than in the breathing zone, and for fields below a certain size, the plume centerline stays below the breathing zone for downwind distances that are longer than 10 ft.

[e] Application rate that approximately corresponds to the rate used at the 50th percentile of all applications in a recent 5-year interval (2003 – 2007) involving products containing 94 – 100% chloropicrin. Concentrations corresponding to these rates are informational only, as current product labels exceed these rates.

Table A3-9. Chloropicrin Off-Site Air Concentrations Estimated for Bedded Non-Tarped Applications to a 15-Acre Square Field [a]

Distance from Edge of 15-Acre Square Field	Application Rate (lbs/Acre) [b]	1-Hour, Day ($\mu g/m^3$)	1-Hour, Night ($\mu g/m^3$)	6-Hour, Day ($\mu g/m^3$)	6-Hour, Night ($\mu g/m^3$)	24-Hour ($\mu g/m^3$)
Current Maximum [c]						
10 feet (3.0 meters)	250	34,000	49,000	14,000	20,000	4,200
50 feet (15 meters)	250	33,000	51,000 [d]	13,000	21,000 [d]	3,800
100 feet (30 meters)	250	29,000	49,000	12,000	20,000	3,200
300 feet (91 meters)	250	19,000	38,000	7,900	15,000	2,000
500 feet (152 meters)	250	15,000	31,000	6,100	12,000	1,500
1,320 feet (402 meters)	250	8,500	18,000	3,500	7,400	780
2,500 feet (760 meters)	250	5,300	12,000	2,200	5,000	410
50th Percentile [e]						
10 feet (3.0 meters)	150	20,000	29,000	8,300	12,000	2,500
50 feet (15 meters)	150	20,000	30,000 [d]	8,000	12,000	2,300
100 feet (30 meters)	150	17,000	30,000	7,000	12,000	1,900
300 feet (91 meters)	150	12,000	23,000	4,700	9,300	1,200
500 feet (152 meters)	150	9,000	18,000	3,700	7,500	920
1,320 feet (402 meters)	150	5,100	11,000	2,100	4,400	470
2,500 feet (760 meters)	150	3,200	7,400	1,300	3,000	250

[a] From Barry (2009), based on data from Beard *et al*. (1996), except for bedded drip tarp by Rotondaro (2004). Concentrations were generated with the Industrial Source Complex Short Term Version 3 (ISCST3) air dispersion model, and have been rounded to two significant figures. The concentrations assumed a receptor 1.2 m above ground and 10 ft (3.0 m) from the edge of a square, 15-acre (6.1-ha) treated area. Multiply value by 0.1487 to get result in parts per billion (ppb).

[b] Multiply value by 1.123 to get rate in kilograms per hectare (kg/ha).

[c] This application rate is the maximum allowed for that method on any product label currently registered in California.

[d] In some cases concentrations are lower at 10 ft than at 50 ft because concentrations are estimated in the breathing zone rather than at ground level. A the field edge, concentrations are higher at ground level than in the breathing zone, and for fields below a certain size, the plume centerline stays below the breathing zone for downwind distances that are longer than 10 ft.

[e] Application rate that approximately corresponds to the rate used at the 50th percentile of all applications in a recent 5-year interval (2003 – 2007) involving products containing 94 – 100% chloropicrin, assuming that all applications were bedded applications reported in the Pesticide Use Report at effective broadcast rates; no information is available about the validity of this assumption. Concentrations corresponding to these rates are informational only, as (with the exception of bedded drip tarped applications) current product labels exceed these rates.

Table A3-10. Chloropicrin Off-Site Air Concentrations Estimated for Bedded Tarped Applications to a 15-Acre Square Field [a]

Distance from Edge of 15-Acre Square Field	Application Rate (lbs/Acre) [b]	1-Hour, Day ($\mu g/m^3$)	1-Hour, Night ($\mu g/m^3$)	6-Hour, Day ($\mu g/m^3$)	6-Hour, Night ($\mu g/m^3$)	24-Hour ($\mu g/m^3$)
Current Maximum [c]						
10 feet (3.0 meters)	500	35,000	56,000	14,000	23,000	6,200
50 feet (15 meters)	500	34,000	58,000 [d]	14,000	24,000 [d]	5,600
100 feet (30 meters)	500	30,000	56,000	12,000	23,000	4,700
300 feet (91 meters)	500	20,000	43,000	8,300	18,000	3,000
500 feet (152 meters)	500	16,000	35,000	6,400	14,000	2,300
1,320 feet (402 meters)	500	8,900	21,000	3,600	8,500	1,200
2,500 feet (760 meters)	500	5,600	14,000	2,300	5,800	600
50^{th} Percentile [e]						
10 feet (3.0 meters)	150	11,000	17,000	4,300	6,900	1,900
50 feet (15 meters)	150	10,000	17,000	4,200	7,100 [d]	1,700
100 feet (30 meters)	150	9,100	17,000	3,700	6,900	1,400
300 feet (91 meters)	150	6,100	13,000	2,500	5,300	890
500 feet (152 meters)	150	4,700	11,000	1,900	4,300	680
1,320 feet (402 meters)	150	2,700	6,200	1,100	2,500	350
2,500 feet (760 meters)	150	1,700	4,200	680	1,700	180

[a] From Barry (2009), based on data from Beard *et al*. (1996), except for bedded drip tarp by Rotondaro (2004). Concentrations were generated with the Industrial Source Complex Short Term Version 3 (ISCST3) air dispersion model, and have been rounded to two significant figures. The concentrations assumed a receptor 1.2 m above ground and 10 ft (3.0 m) from the edge of a square, 15-acre (6.1-ha) treated area. Multiply value by 0.1487 to get result in parts per billion (ppb).

[b] Multiply value by 1.123 to get rate in kilograms per hectare (kg/ha).

[c] This application rate is the maximum allowed for that method on any product label currently registered in California.

[d] In some cases concentrations are lower at 10 ft than at 50 ft because concentrations are estimated in the breathing zone rather than at ground level. A the field edge, concentrations are higher at ground level than in the breathing zone, and for fields below a certain size, the plume centerline stays below the breathing zone for downwind distances that are longer than 10 ft.

[e] Application rate that approximately corresponds to the rate used at the 50^{th} percentile of all applications in a recent 5-year interval (2003 – 2007) involving products containing 94 – 100% chloropicrin, assuming that all applications were bedded applications reported in the Pesticide Use Report at effective broadcast rates; no information is available about the validity of this assumption. Concentrations corresponding to these rates are informational only, as (with the exception of bedded drip tarped applications) current product labels exceed these rates.

Table A3-11. Chloropicrin Off-Site Air Concentrations Estimated for Broadcast Tarped Applications to a 15-Acre Square Field [a]

Distance from Edge of 15-Acre Square Field	Application Rate (lbs/Acre) [b]	1-Hour, Day ($\mu g/m^3$)	1-Hour, Night ($\mu g/m^3$)	6-Hour, Day ($\mu g/m^3$)	6-Hour, Night ($\mu g/m^3$)	24-Hour ($\mu g/m^3$)
Current Maximum [c]						
10 feet (3.0 meters)	500	32,000	6,800	13,000	2,800	3,600
50 feet (15 meters)	500	31,000	7,000 [d]	13,000	2,900 [d]	3,300
100 feet (30 meters)	500	28,000	6,800	11,000	2,800	2,700
300 feet (91 meters)	500	19,000	5,200	7,600	2,100	1,700
500 feet (152 meters)	500	14,000	4,200	5,900	1,700	1,300
1,320 feet (402 meters)	500	8,100	2,500	3,300	1,000	680
2,500 feet (760 meters)	500	5,100	1,700	2,100	700	360
50th Percentile [e]						
10 feet (3.0 meters)	150	9,700	2,000	4,000	830	1,100
50 feet (15 meters)	150	9,400	2,100 [d]	3,800	860 [d]	980
100 feet (30 meters)	150	8,300	2,000	3,400	830	820
300 feet (91 meters)	150	5,600	1,600	2,300	640	520
500 feet (152 meters)	150	4,300	1,300	1,800	520	400
1,320 feet (402 meters)	150	2,400	750	990	310	200
2,500 feet (760 meters)	150	1,500	510	620	210	110

[a] From Barry (2009), based on data from Beard *et al*. (1996), except for bedded drip tarp by Rotondaro (2004). Concentrations were generated with the Industrial Source Complex Short Term Version 3 (ISCST3) air dispersion model, and have been rounded to two significant figures. The concentrations assumed a receptor 1.2 m above ground and 10 ft (3.0 m) from the edge of a square, 15-acre (6.1-ha) treated area. Multiply value by 0.1487 to get result in parts per billion (ppb).

[b] Multiply value by 1.123 to get rate in kilograms per hectare (kg/ha).

[c] This application rate is the maximum allowed for that method on any product label currently registered in California.

[d] In some cases concentrations are lower at 10 ft than at 50 ft because concentrations are estimated in the breathing zone rather than at ground level. A the field edge, concentrations are higher at ground level than in the breathing zone, and for fields below a certain size, the plume centerline stays below the breathing zone for downwind distances that are longer than 10 ft.

[e] Application rate that approximately corresponds to the rate used at the 50th percentile of all applications in a recent 5-year interval (2003 – 2007) involving products containing 94 – 100% chloropicrin. Concentrations corresponding to these rates are informational only, as current product labels exceed these rates.

Table A3-12. Chloropicrin Off-Site Air Concentrations Estimated for Bedded Drip Tarped Applications to a 15-Acre Square Field [a]

Distance from Edge of 15-Acre Square Field	Application Rate (lbs/Acre) [b]	1-Hour, Day ($\mu g/m^3$)	1-Hour, Night ($\mu g/m^3$)	6-Hour, Day ($\mu g/m^3$)	6-Hour, Night ($\mu g/m^3$)	24-Hour ($\mu g/m^3$)
Current Maximum [c]						
10 feet (3.0 meters)	300	9,100	1,500	3,700	620	940
50 feet (15 meters)	300	8,800	1,600 [d]	3,600	640 [d]	840
100 feet (30 meters)	300	7,800	1,500	3,200	620	700
300 feet (91 meters)	300	5,200	1,200	2,100	480	450
500 feet (152 meters)	300	4,100	940	1,700	380	340
1,320 feet (402 meters)	300	2,300	560	940	230	170
2,500 feet (760 meters)	300	1,400	380	580	160	91
50th Percentile [e]						
10 feet (3.0 meters)	150	4,600	760	1,900	310	470
50 feet (15 meters)	150	4,400	780 [d]	1,800	320 [d]	420
100 feet (30 meters)	150	3,900	760	1,600	310	350
300 feet (91 meters)	150	2,600	580	1,100	240	220
500 feet (152 meters)	150	2,000	470	830	190	170
1,320 feet (402 meters)	150	1,100	280	470	110	87
2,500 feet (760 meters)	150	720	190	290	77	45

[a] From Barry (2009), based on data from Beard *et al*. (1996), except for bedded drip tarp by Rotondaro (2004). Concentrations were generated with the Industrial Source Complex Short Term Version 3 (ISCST3) air dispersion model, and have been rounded to two significant figures. The concentrations assumed a receptor 1.2 m above ground and 10 ft (3.0 m) from the edge of a square, 15-acre (6.1-ha) treated area. Multiply value by 0.1487 to get result in parts per billion (ppb).

[b] Multiply value by 1.123 to get rate in kilograms per hectare (kg/ha).

[c] This application rate is the maximum allowed for that method on any product label currently registered in California.

[d] In some cases concentrations are lower at 10 ft than at 50 ft because concentrations are estimated in the breathing zone rather than at ground level. A the field edge, concentrations are higher at ground level than in the breathing zone, and for fields below a certain size, the plume centerline stays below the breathing zone for downwind distances that are longer than 10 ft.

[e] Application rate that approximately corresponds to the rate used at the 50th percentile of all applications in a recent 5-year interval (2003 – 2007) involving products containing 94 – 100% chloropicrin, assuming that all applications were bedded applications reported in the Pesticide Use Report at effective broadcast rates; no information is available about the validity of this assumption.

APPENDIX 4. OFF-SITE CHLOROPICRIN CONCENTRATIONS ESTIMATED FOR TWO-DAY ROLLING APPLICATIONS

Table A4-1. Chloropicrin Off-Site Air Concentrations Estimated for Two Sequential Application Days at a Distance of 10 Feet (3.0 Meters) from the Edge of the Field [a]

Application Method	Study Location	Maximum Application Rate (lbs/Acre) [b]	6-Hour, Day ($\mu g/m^3$)	6-Hour, Night ($\mu g/m^3$)	24-Hour ($\mu g/m^3$)
Current Day [c]					
Broadcast non-tarped	Arizona	500	7,500	**44,000**	6,500
Bedded non-tarped	Arizona	250	17,000	27,000	5,000
Bedded tarped	Arizona	500	**18,000**	31,000	**7,400**
Broadcast tarped	Arizona	500	16,000	3,800	4,300
Bedded drip tarped	California	300	4,700	840	1,100
Previous Day [d]					
Broadcast non-tarped	Arizona	500	**14,000**	24,000	7,200
Bedded non-tarped	Arizona	250	10,000	17,000	5,100
Bedded tarped	Arizona	500	16,000	**33,000**	**8,100**
Broadcast tarped	Arizona	500	10,000	19,000	5,100
Bedded drip tarped	California	300	2,400	4,200	1,200
Total [e]					
Broadcast non-tarped	Arizona	500	22,000	**68,000**	14,000
Bedded non-tarped	Arizona	250	27,000	44,000	10,000
Bedded tarped	Arizona	500	**34,000**	64,000	**16,000**
Broadcast tarped	Arizona	500	26,000	23,000	9,400
Bedded drip tarped	California	300	7,100	5,000	2,300

[a] From Barry (2008c), based on data from Beard *et al.* (1996), except for bedded drip tarp by Rotondaro (2004). Concentrations were generated with the Industrial Source Complex Short Term Version 3 (ISCST3) air dispersion model, and have been rounded to two significant figures. Bolded values represent the highest concentration for each interval.

[b] This application rate is the maximum allowed for that method on any product label currently registered in California. Multiply value by 1.123 to get rate in kilograms per hectare (kg/ha).

[c] The concentrations assumed a receptor 1.2 m above ground and 10 ft (3.0 m) from the edge of a square, 40-acre treated area, in the first 24 hours of a fumigation.

[d] A second field, also 40 acres and square, and treated the previous day, is assumed to be upwind of the field treated during the current day. Note that in some cases higher concentrations occur on the day after application than on the day of application (i.e., previous day's concentration may be higher than current day's).

[e] Concentrations are assumed to be additive. For example, 7,500 + 14,000 = 21,500 (rounded to 22,000 for total concentration).